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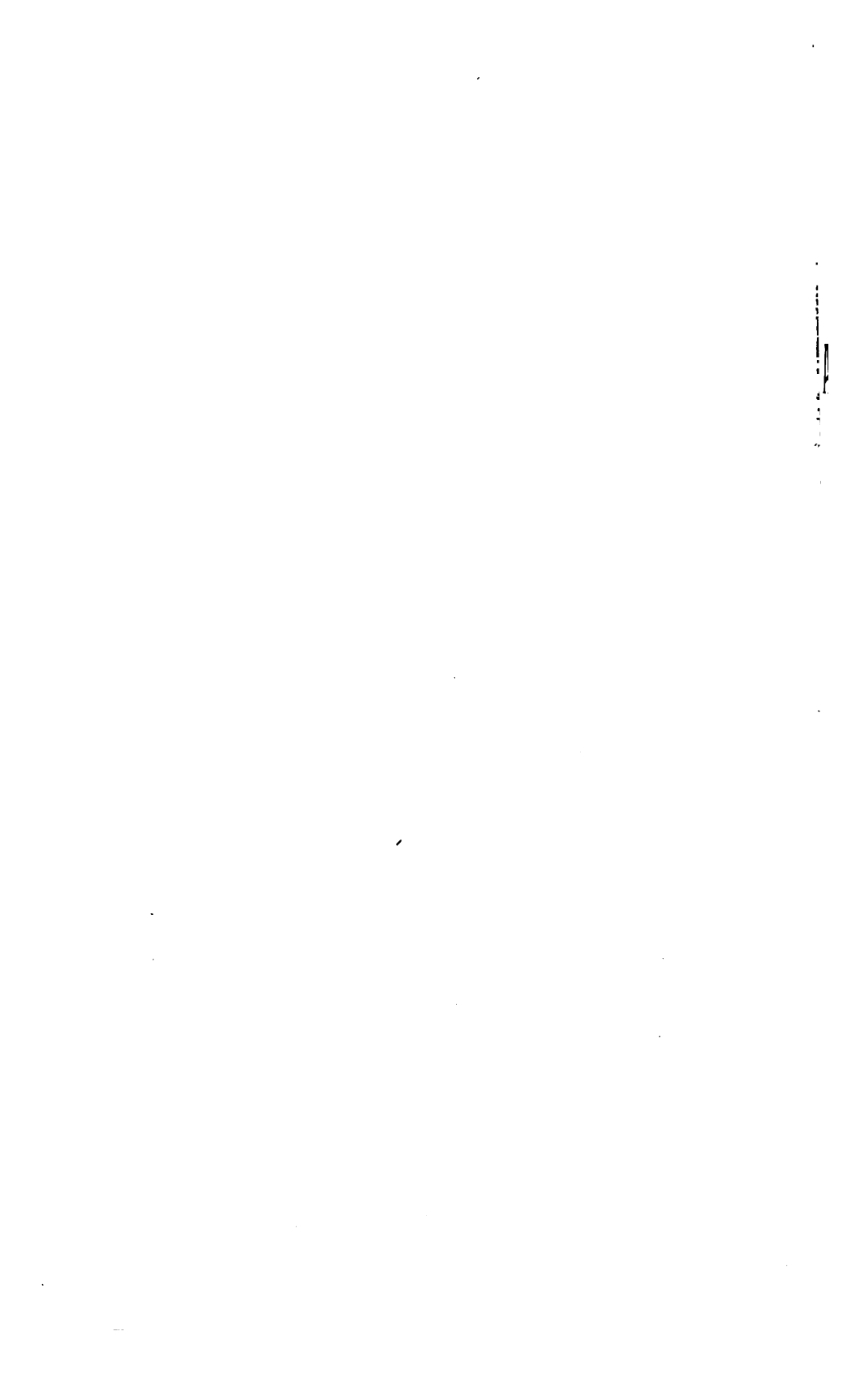
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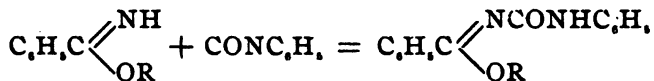
[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON UREAIMIDO ESTERS, THIOUREAIMIDO ESTERS, ACYL-THIOUREAIMIDO ESTERS, AND UREAAMIDINES.

[PRELIMINARY PAPER.]

BY HENRY L. WHEELER AND W. MURRAY SANDERS.

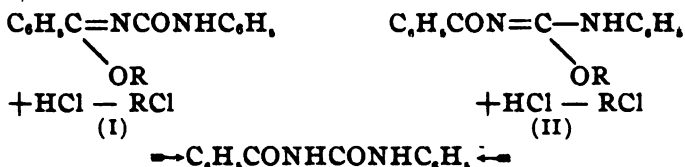
REPRESENTATIVES of new classes of compounds, isomeric or metamerie with the acylpseudourea ethers, acylpseudothiurea ethers and diacylpseudothiurea ethers, can be prepared by combining isocyanates, mustard oils, and acyl rhodanides with imido esters. The imido esters immediately combine with phenyl isocyanate, at ordinary temperatures, giving a quantitative yield of an addition product as follows:



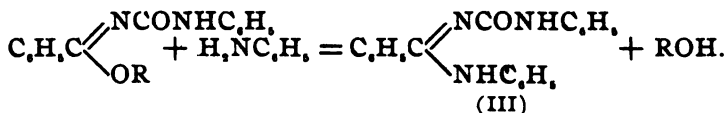
This class of compounds, perhaps, may be called urea-imido esters or carbamidimido esters, since they have the structure of imido esters and ureas combined. They are extremely sensitive towards hydrogen chloride by which reagent, just as the acylpseudourea ethers¹ (II) they are readily and quantitatively converted in the cold, with loss of alkyl chloride, into acylureas.

¹ Stieglitz and Dains: This Journal, 21, 136.

This reaction with these two classes of compounds proceeds as follows:

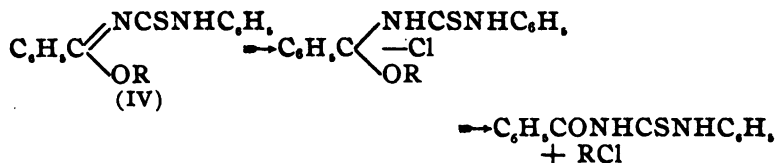


It will be noticed that the imido ester grouping in the different positions in these isomers are affected alike, inasmuch as under similar conditions both compounds give with hydrogen chloride the same derivative, benzoylphenylurea. The ureaimido esters (I) readily react with aniline, at the temperature of the steam-bath, and ureaamidines are formed as follows:



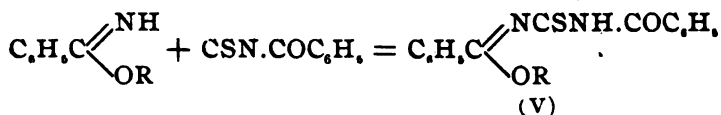
Whether the structure shown in formula (III) or the tautomeric form is to be assigned to these amidines must be decided later. These amidines have little or no basic properties.

The mustard oils, phenylmustard oil and allyl mustard oil, react less energetically than phenyl isocyanate with the imido esters. On long standing or on warming, the mixtures deposit crystals. These compounds, for which the name thioureaimido esters (IV) is proposed, are closely similar to the above oxygen analogues, since with hydrogen chloride, under similar conditions, they readily separate alkyl chloride and give the corresponding acylthio ureas. The mechanism of the reaction is as follows:

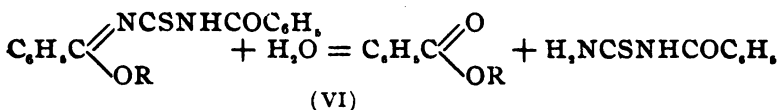


The isomeric acylpseudothiourea ethers and the diacylpseudothiourea ethers apparently have not yet been prepared, so that a comparison of the behavior of these compounds with the thioureaimido ester derivatives must be deferred to a later date.

When the thioureaimido esters are warmed with aniline, and other organic bases, thioureaimidines are formed. Like the above ureaamidines they appear to have no basic properties. The fact that they are not soluble in alkali affords new evidence that the double union of the imido ester grouping confers a basic nature to the molecules. Here, however, it is neutralized by the negative character of the urea group. The imido esters combine with acetyl and benzoyl thiocyanates with evolution of heat, the mixtures readily solidifying. Acylthioureaimido esters (V) are then produced, as follows:



These compounds are formed more readily than the above and they are far more unstable than the thioureaimido esters. When they are warmed with hydrochloric acid they decompose in a different manner from the other types of ureaimido esters. A monoacylthiourea, and not a diacyl derivative, is obtained. The decomposition under this treatment takes place at the double union as follows:



What appears to be the nearest known analogue to a metamer of the above or dibenzoylpseudothiurea ether is the ethylisodicarbethoxyurea, $\text{C}_2\text{H}_5\text{O.CON}=\text{C} \begin{array}{l} \text{NCO.COC}_2\text{H}_5 \\ \diagup \\ \text{OC}_2\text{H}_5 \end{array}$, of Dains.¹ This

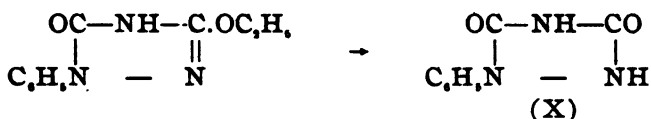
compound is also very sensitive towards hydrogen chloride; however, it does not separate at the double union, like the above, but decomposes with the evolution of ethyl chloride, giving the diacylurea, $\text{C}_2\text{H}_5\text{OCONHCONHCO.COC}_2\text{H}_5$. The ease with which the ureaimido esters decompose with hydrochloric acid, without forming a stable intermediate addition product or "salt," recalls the perfectly analogous behavior of the acylimido esters.² In the case of the latter, the above two reactions with

¹ *Loc. cit.*

² Wheeler, Walden and Metcalf: *Am. Chem. J.*, 19, 129 and 20, 64.

³ *J. prakt. Chem.*, 10, 118.

ethoxy-5-triazolon, and that it has the structure represented by formula (IX), is shown by its behavior, on boiling with strong hydrochloric acid, whereupon it is converted into Pinner's¹ urazole, (X):



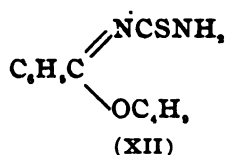
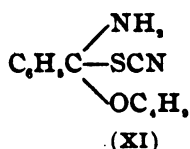
The process which in general serves for the preparation of simple or monosubstituted ureas and thioureas, and which consists of treating a salt of an amine with potassium cyanate or thiocyanate, does not lead to the formation of the prototypes of the above urea derivatives, when applied to the salts of the imido esters. This fact seems to the writer to be a strong argument in support of the theory of Stieglitz that the salts of the imido esters are not ammonium derivatives, but that they are derived

from the form $\text{RC} \begin{array}{l} \nearrow \text{NH}_2 \\ \searrow \text{OR} \end{array} \text{Cl}$, etc. In fact, the properties of the cyanic

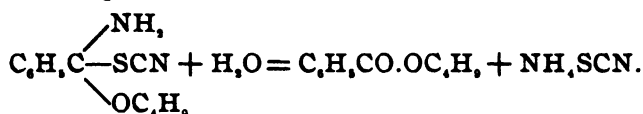
and thiocyanic acid salts do not agree with those which would be expected for salts having an ammonium structure.

When ice-cold solutions of benzimidobutyl ester hydrochloride and potassium cyanate, in molecular proportions, are mixed together, a mass of well-crystallized, colorless prisms separate. If an attempt is made to filter these at ordinary temperature they rapidly decompose, giving off a gas (CO_2 ?), and completely liquefying. Owing to the unstable nature of this salt, which is undoubtedly a cyanate, it was not examined further. On the other hand, the corresponding thiocyanic salt is far more stable. It can be prepared, at ordinary temperature, by mixing solutions of the imido ester hydrochloride with potassium thiocyanate, whereupon a bulky mass of colorless prisms or needles separate. This salt has the structure represented by formula (XI), and all attempts to rearrange it into the metameric thioureaimid ester (XII) failed.

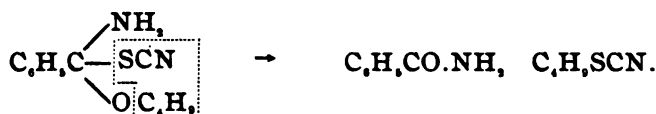
¹ *Ber. d. chem. Ges.*, 21, 1219.



When this salt is warmed in aqueous solution it dissolves, but the solution almost immediately becomes turbid and an oil (isobutyl benzoate) separates. On evaporating to dryness nothing but ammonium thiocyanate is obtained. The decomposition then proceeds as follows :



If the dry salt is heated above its melting-point it decomposes smoothly as follows :



It will be noticed that these reactions are analogous in every respect to those of the hydrochloric acid salts of the imido esters.

EXPERIMENTAL PART.



Phenyl isocyanate (3.4 grams) and benzimidoisobutyl ester (10 grams) combined with evolution of heat and the mixture solidified to a white mass. When this was crystallized from alcohol, colorless prisms were obtained which melted from 99°–100°. A nitrogen determination gave :

	Calculated for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$.	Found.
Nitrogen.....	9.4	9.1

Action with Hydrogen Chloride.—Some of the above material was dissolved in benzene and the solution was saturated with hydrogen chloride whereupon colorless prisms separated, melting at about 200°. This material proved to be *Benzoylphenylurea*, $\text{C}_6\text{H}_5\text{CONHCONHC}_6\text{H}_5$, which crystallized from alcohol in long

silky needles, and on boiling it with sodium hydroxide it gave phenylurea.

The extreme sensitiveness of compounds of this type towards hydrochloric acid was shown by the fact that it was found to be impossible to isolate ureaimido esters from benzimidomethyl, ethyl, and phenylacetimidomethyl esters and phenyl isocyanate, if the latter contained phosphorus oxychloride. Under these conditions the benzimido esters gave *benzoylphenylurea*, while phenylacetimidomethyl ester gave a compound very difficultly soluble in alcohol. It crystallized in the form of needles and melted at 166° and a nitrogen determination showed that it was *phenylacetylphenylurea*, $C_6H_5CH_2CONHCONHC_6H_5$:

	Calculated for $C_{18}H_{14}N_2O_2$	Found.
Nitrogen.....	11.0	11.0

Action with Aniline.—Phenylureaimidoisobutyl benzoate (2 grams) and aniline (0.6 gram), were mixed in benzene and warmed on the water-bath whereupon a substance separated in granular crystals. It was found to be very difficultly soluble in alcohol (a property of ureaamidines, which is general as far as we have observed, and on boiling with alcohol it melted from 179°–180°. A nitrogen determination agreed with the figures calculated for *benzenylphenylureaphenylamidine*, $C_6H_5NH-(C_6H_5)C=NCONHC_6H_5$.

	Calculated for $C_{26}H_{17}N_3O$	Found.
Nitrogen.....	13.3	13.0

This amidine is insoluble in dilute hydrochloric acid and no hydrochloric acid salt was obtained when the material was dissolved in benzene and saturated with hydrogen chloride. It is insoluble in alkali.



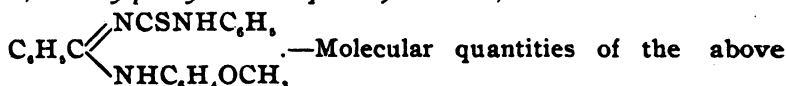
Equal quantities of benzimidomethyl ester and phenyl mustard oil (5 grams of each) were mixed and kept at a temperature of about 60°–70° for two days. On cooling, then, the mixture solidified almost completely. In each of the experiments with phenyl mustard oil and the imido esters, a yellow mixture resulted although the ingredients before mixing were colorless.

On crystallizing from alcohol beautiful colorless or cream-colored lozenge-shaped tables were obtained which melted sharply at 132° . The material is readily soluble in benzene and hot alcohol, difficultly in cold alcohol, and a nitrogen determination gave:

	Calculated for $C_{12}H_{14}N_2OS$.	Found.
Nitrogen.....	10.37	10.29

When this compound was treated with cold dilute hydrochloric acid, in which it is insoluble, little or no action was observed after two days' standing. When a little alcohol was added and the whole was warmed, effervescence took place, methyl chloride was evolved, and, on cooling, the long characteristic colorless needles of *benzoylphenylthiourea*, $C_6H_5CONHC_6H_5$, were obtained, melting about 148° .

Benzoylphenylthiourea-p-anisylamidine,



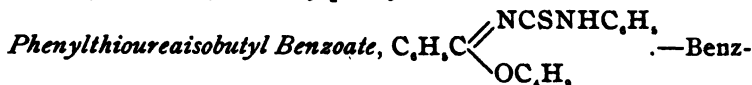
imido ester and *p*-anisidine were mixed in benzene solution and allowed to stand at a temperature of about 70° for several hours, whereupon a mass of plates or scales separated. This material was very difficultly soluble in alcohol and in benzene. When crystallized from these solvents and from amyl acetate, it melted at about 180° . A satisfactory nitrogen determination was not obtained, undoubtedly owing to the fact that this substance, as well as the corresponding phenyl and naphthyl amidines, burn with great difficulty, the results invariably coming low.



Benzimidoethylester (5 grams) and phenyl mustard oil (4.5 grams) gave a yellow oil directly on mixing. After two days the material solidified to a glistening mass of flattened prisms or tables and on crystallizing from alcohol it separated in the form of cream-colored tables and it melted sharply at 119° . These thiourea-imido esters, in general, show a great tendency to crystallize. A nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2OS$.	Found.
Nitrogen.....	9.8	9.7

When treated with hydrochloric acid it behaved precisely like the methyl ester and benzoylphenylthiourea was obtained.



imidoisobutyl ester (5 grams) and phenyl mustard oil (3.8 grams) behaved, on mixing and standing, precisely like the above. When crystallized from alcohol it forms large, stout tables and it melts at 125° . A nitrogen determination gave:

	Calculated for $C_{18}H_{20}N_2OS$.	Found.
Nitrogen.....	8.9	8.9

When this was treated with hydrochloric acid and warmed, *benzoylphenylthiourea* was obtained.

When 2 grams of this imido ester were warmed on the water-bath with aqueous-alcoholic ammonia for a number of hours and then allowed to cool, colorless crystals separated melting from 151° – 153° . A nitrogen determination gave 18.5 per cent., while the calculated for benzenylphenylthiourea amidine is 27.0 per cent., and that for phenylthiourea which melts at 154° is 18.4 per cent. The material, in fact, had the bitter taste and other properties of *phenylthiourea*.

When this thioureaimido ester was treated with methyl iodide a varnish was obtained which crystallized after long standing.

Phenylthioureaisobutyl benzoate readily reacts with phenyl hydrazine, giving off hydrogen sulphide and it gives a compound which crystallizes in plates when treated with benzoyl chloride. These reactions will receive more thorough attention later.



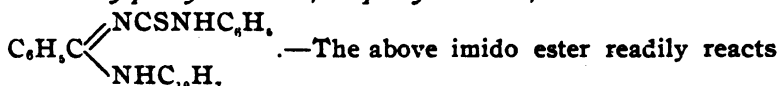
The above imido ester (4 grams) and aniline (1.1 grams) after warming on the water-bath gave off only a trace of hydrogen sulphide. The product, on crystallizing from alcohol, formed a beautiful mass of large thin plates. They melted from 151° – 152° and a nitrogen determination gave:

	Calculated for $C_{20}H_{17}N_3S$.	Found.
Nitrogen.....	12.6	12.0

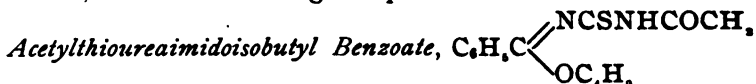
This material is insoluble in cold hydrochloric acid, concen-

trated or dilute. On warming, it dissolves, but on cooling it crystallizes out again unaltered. Platinum chloride precipitates a curdy yellow mass from the concentrated hydrochloric acid solution.

Benzenylphenylthiourea-β-naphthylamidine,



with β-naphthylamine, giving a compound that crystallizes in minute plates and which is extremely insoluble in the ordinary organic solvents; when crystallized from alcohol and amyl acetate it melted, not sharply, from 182°–183°. The material burned very slowly and a satisfactory nitrogen determination was not obtained, the calculated being 11.0 per cent. while 10.0 was found.



—Benzimidoisobutyl ester and acetyl thiocyanate combine with evolution of considerable heat and, on cooling, the mixture completely solidifies, whereupon, on crystallizing from alcohol, colorless needles are obtained which melt from 125°–126°. A nitrogen determination gave:

	Calculated for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$.	Found
Nitrogen.....	10.0	9.9

When this imido ester was treated in alcoholic solution with hydrogen chloride a compound was obtained melting at 166° and which had all the properties of *acetylthiourea*, $\text{CH}_3\text{CONHCSNH}_2$.

With phenylhydrazine it evolves hydrogen sulphide, and on crystallizing the product from alcohol acetylthiourea separates.



—When benzimidoethyl ester (6.1 grams) was mixed with 5.6 grams of benzoyl sulphocyanate the mixture completely solidified. On crystallizing from alcohol, needles were obtained which melted from 131°–132°, and on analysis the following result was obtained:

	Calculated for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$.	Found.
Nitrogen	8.9	8.8

When this imido ester was warmed with phenylhydrazine the only crystalline material obtained was *benzoylthiourea*.

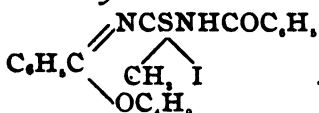


—When benzimidoisobutyl ester (10 grams) and benzoyl sulphocyanate (7.4 grams) were mixed, considerable heat was evolved and the mass solidified. When this was crystallized from alcohol, colorless needles, melting at 120° were obtained. A nitrogen determination gave :

	Calculated for $C_{19}H_{20}N_2O_4S$.	Found.
Nitrogen	8.2	8.4

When this imido ester was treated with hydrogen chloride in benzene solution, *benzoylthiourea*, melting at 169° – 170° was obtained. Apparently this same compound was obtained when the ester was treated with ammonia, phenylhydrazine and with benzoyl chloride. These results show the great tendency this ester has to separate at the double bond.

*Benzoylthiourea*imidoisobutyl Benzoate Methyl Iodide,



—The above imido ester and methyl

iodide combine in benzene solution to form a compound containing iodine and which crystallizes from alcohol in well-developed, colorless prisms melting from 204° – 205° . A nitrogen determination gave :

	Calculated for $C_{20}H_{22}N_2O_4SI$.	Found.
Nitrogen	5.7	5.7



—When molecular proportions of the above imido ester and aniline were heated in benzene solution a substance was obtained which crystallized in colorless prisms and which melted from 145° – 146° . A nitrogen determination gave :

	Calculated for $C_{21}H_{17}N_3OS$.	Found.
Nitrogen	11.6	11.2

No hydrochloric acid salt was obtained when this amidine was treated with hydrogen chloride.

Benzenylbenzoylthioureaorthotolylamidine,

$$\text{C}_6\text{H}_5\text{C} \begin{array}{l} \nearrow \text{NCSNHCOC}_6\text{H}_5 \\ \searrow \text{NHC}_6\text{H}_4\text{CH}_3 \end{array}$$
 .—This compound was obtained on fusing the imido ester with ortho toluidine. It crystallized from alcohol in colorless prisms which melted from 116°–117° and a nitrogen determination gave :

	Calculated for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{OS}$.	Found
Nitrogen.....	11.2	10.8

Benzoylthioureaimidomethylphenyl Acetate,

$$\text{C}_6\text{H}_5\text{CH}_2\text{C} \begin{array}{l} \nearrow \text{NCSNHCOC}_6\text{H}_5 \\ \searrow \text{OCH}_3 \end{array}$$
 .—When phenylacetimidomethyl ester (5.6 grams) was treated with benzoylthiocyanate (5 grams), the mixture solidified immediately. It was crystallized from alcohol and obtained in the form of colorless needles melting from 116°–117°. A nitrogen determination gave :

	Calculated for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$.	Found.
Nitrogen	8.9	9.3

When this imido ester was treated with phenylhydrazine, hydrogen sulphide was evolved but the product, on crystallizing from alcohol, was neither an amidine or a triazole. It contained 15.4 per cent. of nitrogen while the calculated for *benzoylthiourea* is 15.5 per cent. It agreed in all its properties with the acylthiourea.

Benzoylthioureaimidoethylphenyl Acetate,

$$\text{C}_6\text{H}_5\text{CH}_2\text{C} \begin{array}{l} \nearrow \text{NCSNHCOC}_6\text{H}_5 \\ \searrow \text{OC}_2\text{H}_5 \end{array}$$
 ; was prepared from phenylacetimidoethyl ester. It forms colorless needles from alcohol which melt from 140°–141°. When treated with hydrogen chloride in alcoholic solution it gave small prismatic crystals, melting from 169°–170°, and a nitrogen determination agreed with the calculated for benzoylthiourea :

	Calculated for $\text{C}_9\text{H}_8\text{N}_2\text{SO}$.	Found.
Nitrogen	15.5	15.6

The Thiocyanic Acid Salt of Benzimidoisobutyl Ester,

$$\text{C}_6\text{H}_5\text{C} \begin{array}{l} \nearrow \text{NH}_2 \\ \text{---} \text{SCN} \\ \searrow \text{OC}_2\text{H}_5 \end{array}$$
 is readily formed on mixing aqueous solutions

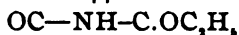
of the imido ester hydrochloride and potassium cyanate. It then separates as a mass of colorless needles or prisms which are quite difficultly soluble in water. It melts at about 130° . A portion dried in a desiccator over calcium chloride and then for a few minutes at 60° – 70° gave the following results on analysis:

	Calculated for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{SO}$.	Found.
Nitrogen.....	11.8	11.9

Its reaction with iron chloride and with alkali showed that this material was a salt of the imido ester and not the isomeric thioureaimidoisobutyl benzoate. It decomposes on warming with water smoothly into ammonium thiocyanate and isobutyl benzoate and when heated above its melting-point it gives benzamide and isobutyl thiocyanate.

EXPERIMENTS BY BAYARD BARNES.

Carbethoxythioncarbamic Ester, $\text{C}_6\text{H}_5\text{OCONHCS.OC}_2\text{H}_5$.—This was prepared according to the directions of Delitsch;¹ when purified by means of its potassium salt, it was found to boil unaltered at 135° at 13 mm. pressure. It melts at 44° .



1-Phenyl-3-ethoxy-5-triazolone, $\text{C}_6\text{H}_5\text{N}=\text{N}$, was obtained when the above carbamic ester (15 grams) was heated with phenylhydrazine (9 grams) on the steam-bath. After the evolution of hydrogen sulphide and alcohol had ceased, the material was crystallized from hot water, whereupon colorless needles, melting from 150° – 151° , were obtained. This material was soluble in alkali and was precipitated unaltered by acids. It contained no sulphur and on analysis the following results were obtained:

	Calculated for $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_2$.	Found.
Carbon	58.5	58.9
Hydrogen	5.2	5.3
Nitrogen	20.5	20.4

¹ *J. prakt. Chem.*, 10, 118.

When this compound was boiled for some time with concentrated hydrochloric acid and alcohol, colorless plates were obtained, which melted at 263° , showing signs of melting at 255° . For purposes of comparison Pinner's¹ urazole was prepared and it was found to be identical with the above.

Acetylphenylurethane, $\text{CH}_3\text{CO}(\text{C}_6\text{H}_5)\text{NCO}.\text{OC}_6\text{H}_5$.—Ten grams of phenylurethane were boiled with an equal weight of acetic anhydride for several hours whereupon, on pouring into water, unaltered urethane was obtained. Acetyl chloride was then added and boiled for about one hour. Then about one-half of the solution was distilled off at ordinary pressure and the remainder at 10 mm. pressure whereupon the material practically all boiled from 142° – 143° . It was thus obtained as a colorless oil which, like formylphenylurethane, refused to solidify on cooling. A nitrogen determination gave :

	Calculated for $\text{C}_{11}\text{H}_{14}\text{NO}_3$	Found.
Nitrogen.....	6.7	7.3

When this compound was gently warmed with phenylhydrazine and the product was crystallized from benzene, colorless plates, melting at 128° , were obtained. The following nitrogen determination showed that this material was not a triazole derivative but rather *acetylphenylhydrazine* :

	Calculated for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}$	Found.
Nitrogen.....	18.6	18.0

The action of phenylhydrazine on Hugershoff's² *acetylphenylthiocarbamide*, $\text{CH}_3\text{CONHCSNH}\text{C}_6\text{H}_5$, melting at 139° , although some hydrogen sulphide was evolved, did not lead to the formation of a triazole derivative, at least not as the chief product. The material that separated, on crystallizing from alcohol, formed large, four-sided plates melting at 153° and having all the properties of *phenylthiourea*. In other words the action of phenylhydrazine, in this case, removes the acetyl group.

NEW HAVEN, CONN., May 29, 1900.

¹ *Loc. cit.*

² *Ber. d. chem. Ges.*, 32, 3658.

THE NUCLEIC ACID OF THE EMBRYO OF WHEAT AND ITS PROTEIN COMPOUNDS.¹

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received June 16, 1900.

Frankfurt² has estimated the proportion of various constituents of the embryo of wheat and found globulin, 21.62 per cent., and albumose, 13.62 per cent.

O'Brien³ states that the proteids of wheat germs consist of globulins of the myosin-type, coagulating at 55°, soluble in dilute solutions of sodium chloride or magnesium sulphate and precipitated by excess of these salts; globulins of the vitellin type, coagulating at 75°-78° and soluble in dilute solution of sodium chloride, but not precipitated by an excess; proteose; and albumin not coagulating below 80°, soluble in sodium chloride solution, not precipitated by an excess, nor by dialysis, nor by carbonic acid.

As neither of these investigators has given more than a superficial account of the protein⁴ substances found by him in the embryo of wheat, we determined to investigate this subject, in order to learn definitely which of the proteins contained in the wheat kernel are predominant in the embryo, and whether there is any special difference in character between the proteins of the more physiologically active germ and those of the dormant endosperm.

As a result of this investigation we have found that, of the proteids described by one of us⁵ as constituents of the wheat kernel, the albumin (leucosin), the globulin, and the proteose, which in the whole seed are present in small proportions, together constitute a large part of the embryo, and further, that gliadin and glutenin, the principal proteid constituents of the endosperm, are not present in the embryo.

¹ From advance sheets of the Report of the Connecticut Agricultural Experiment Station for 1899, communicated by the authors.

² *Versuchs-Stationen*, 47, 449.

³ *Annals of Botany*, 9, 543.

⁴ In this paper the term protein denotes the basic molecules which, combined with simple acids, form the "simple proteids," and combined with other more complex groups, form the "compound proteids" (Hammarsten, "Text-book of Physiology," translated by Mandel, third edition (1900). The term proteid in this paper includes both of these groups of protein compounds.

⁵ Osborne and Voorhees: *Am. Chem. J.*, 15, 392 (1893).

Although the globulin and leucosin obtained from the whole seed were free from phosphorus, all of our preparations of the globulin, and many of those of the albumin, from the embryo contained various yet considerable quantities of this element, and when digested with pepsin, yielded insoluble products having the characteristics of nuclein. The elementary composition of those preparations of the embryo-albumin which contained no phosphorus, or only traces, was the same as that of leucosin prepared from the whole seed, while the composition of those embryo-albumin preparations which contained phosphorus differed from that of leucosin in proportion to the phosphorus present.

Analyses of different preparations of embryo-globulin showed no agreement, even when corrected for ash.

These facts led us to examine our extracts for nucleic acid, and having found this acid and determined its composition, it was seen that the differences just alluded to disappear if we assume the phosphorus to be present as nucleic acid and calculate the analyses free from this acid and from ash.

In a paper recently published by one of us on "Some Definite Compounds of Protein Bodies" it was shown that many, if not most preparations of so-called native proteids are, in fact, compounds of protein bodies with acids, and it was suggested that nuclealbumins might prove to be similar phosphoric acid compounds.

In that paper it was also shown that the crystallized globulin, edestin, obtained from hemp-seed, forms a compound with one, and another compound with two molecules of hydrochloric acid, both of which are crystalline, and that the preparations of this globulin as commonly obtained are mixtures of these in various proportions. It was also shown that the protein molecule can combine with more than two molecules of acid, so that several multiple compounds of one acid with the same protein molecule can undoubtedly exist.

That our preparations from the wheat-embryo are mixtures of two or more compounds is shown by the variable proportions of phosphorus which they contain. That phosphorus is a chief factor in determining the proportion of nuclein that separates

¹ This Journal, 21, 486.

during pepsin digestion is shown by the fact that the amount of nuclein found is always in close relation to the amount of phosphorus contained in the preparation.

That the preparations are not mixtures of already formed nuclein with ordinary proteid matter is shown by the difference in solubility and behavior of the original preparation from that of the nuclein derived from it.

It would seem, then, that the nuclein obtained by pepsin digestion is not an original constituent of the extract nor of the cells of the embryo, but results through combination of several molecules of nucleic acid with one of protein.

Accordingly we conclude that these phosphorus-containing preparations from the wheat embryo are mixtures of different protein nucleates and that when subjected to pepsin digestion, in consequence of the conversion of a part of the protein substance into proteose, the proportion of nucleic acid to unaltered protein is increased, so that higher acid nucleates are formed which are insoluble in the digestive fluid.

The grounds for these conclusions are given in the following detailed account of our investigation.

The material at our command consisted of a quantity of wheat germs, a specially prepared product of the Pillsbury Mills, from which the bran and endosperm had been thoroughly removed, which was kindly procured for us by Mr. David Chidlow, of Chicago.

The germ meal, which was prepared and sent to us in cold weather, was immediately extracted with petroleum naphtha and ground to a flour.

I. The Nucleic Acid of the Wheat Embryo.

We shall later show that the precipitate produced by saturating the slightly acid aqueous extract of this wheat-embryo meal with sodium chloride contains almost all the phosphorus of the extract. We accordingly extracted a large quantity of the meal with water, saturated the extract with sodium chloride and subjected the precipitate to a vigorous pepsin digestion. We thus obtained a considerable quantity of nuclein from which we prepared nucleic acid in the following manner:

The nuclein was thoroughly washed with water and then

dilute potash solution was added until all the nuclein had dissolved and its solution become faintly alkaline to phenolphthalein.

This solution was cautiously treated with dilute hydrochloric acid until a precipitate was formed, which separated readily from the solution. This was filtered out and the clear filtrate found to yield no precipitate on adding a *little* more acid. A considerable quantity of strong hydrochloric acid was then added, causing a precipitate of nucleic acid, which separated in large flocks that rapidly settled to a coherent layer. The deposit continued to contract and soon became so dense and brittle that it could be ground to a powder even under water. The solution was decanted, the sediment was thoroughly washed, redissolved with alkali and again thrown down by adding acid. Since this last precipitate still contained much coloring-matter, it was again dissolved with alkali and the solution poured into alcohol. This retained the basic coloring-matter and threw down a voluminous precipitate of potassium nucleate, which was thoroughly washed with large quantities of alcohol, dried to remove the alcohol and then dissolved in water and the nucleic acid reprecipitated by an excess of hydrochloric acid. Since all the coloring-matter had not been removed by the preceding treatment, the precipitate was twice dissolved in alkali and precipitated by pouring into a large volume of alcohol. The nucleic acid was then thrown down by gradually adding dilute hydrochloric acid to the solution of the potash salt; after thoroughly washing the precipitated acid with water and with alcohol it was dried over sulphuric acid and found to weigh 10.14 grams.

After drying to constant weight in hydrogen at 100°, its weight remained unchanged on further heating at 110° in air. When thus dried it had the following composition :

	I.	II.
Carbon.....	36.18	36.31
Hydrogen.....	4.48	4.42
Nitrogen.....	16.03	16.10
Phosphorus.....	8.95	8.86
Ash.....	3.52
P ₂ O ₅ in ash.....	2.88
Difference.....	0.64

The ash consisted, chiefly if not wholly, of potassium meta-

phosphate and therefore by subtracting from it the phosphorus pentoxide which it contained, we obtain the amount of inorganic base which had been precipitated as an acid salt together with the free nucleic acid. Calculating our analyses free from this base, we have the following figures :

COMPOSITION OF NUCLEIC ACID.

	Calculated for $C_{81}H_{91}N_9P_2O_{18}$	Found.
Carbon.....	36.16	36.48
Hydrogen.....	4.45	4.48
Nitrogen.....	16.01	16.17
Phosphorus.....	8.89	8.96
Oxygen.....	34.49	33.91
	<hr/> 100.00	<hr/> 100.00

About 2 grams of this preparation were hydrolyzed by heating for an hour and a half in a boiling water-bath with 2 per cent. hydrochloric acid.

On adding ammonia to this solution, a precipitate soon separated which was digested on the water-bath with an excess of ammonia, filtered out, washed, dried over sulphuric acid, and found to weigh 0.27 gram.

This substance gave the murexide reaction and was insoluble in hot ammonia, both of which properties are characteristic of guanin. On analysis this crude guanin was found to contain :

	Calculated for guanin $C_8H_8N_4O$	Found.
Carbon.....	39.74	40.96
Hydrogen.....	3.31	3.67
Nitrogen.....	46.36	45.21
Oxygen.....	10.59	10.16
	<hr/> 100.00	<hr/> 100.00

The solution filtered from the guanin was precipitated by cold ammoniacal silver nitrate and the voluminous, gelatinous precipitate washed, pressed on filter-paper, suspended in water, and decomposed by hydrochloric acid. The solution containing the hydrochloride of another base, was repeatedly evaporated with water to decompose the chloride and the free base found to weigh 0.2272 gram. This was again dissolved in water and the silver salt precipitated from a boiling solution, the silver compound

was decomposed with hydrochloric acid, and the solution of the hydrochloride was evaporated and crystallized.

The substance separated wholly in four-sided prisms, most of which were truncated by planes at right angles.

This hydrochloride was then converted into the picrate by dissolving in water, adding a little ammonia, evaporating to dryness, dissolving in about 100 cc. of water, and precipitating with a 1.1 per cent. solution of picric acid added cautiously. The very voluminous yellow precipitate was quickly filtered out with the help of a pump, washed thoroughly with water, and dried over sulphuric acid. We thus obtained 0.3766 gram of a picrate, which lost nothing on drying at 110° and had the following composition:

	Calculated for adenin picrate, $C_{11}H_8N_8O_7$.	Found.
Carbon.....	36.27	36.07
Hydrogen.....	2.19	2.51
Nitrogen.....	30.77	30.28
Oxygen.....	30.77	31.14
	100.00	100.00

From the behavior of this base and the composition of its picrate, it is evidently adenin. Since this acid yields on hydrolysis the purin bases, guanin and adenin, as well as phosphoric acid, there can be no doubt that it is a true nucleic acid closely related to the guanylic acid recently described by Bang.¹ The facts that we obtained these two bases from the nucleic acid in nearly molecular proportion and that almost all the nitrogen of the acid was recovered in the guanin and adenin separated from it, lead us to believe that both these bases exist together in the acid molecule. If such is the case, our formula already given must be multiplied by 2.5, making it $C_{27.5}H_{20}N_{20}P_2O_{17.5}$. This formula resembles that of guanylic acid, which, calculated to the same basis, is $C_{27.5}H_{20}N_{20}P_2O_{17.5}$. The two acids are different, since Bang's guanylic acid yields a pentose on hydrolysis, whereas we have obtained no evidence that any sugar can be derived from our acid. As we are at present engaged in a study of the reactions and constitution of this acid, we will reserve further statements respecting it for a future paper, which we expect to be able to publish soon.

¹ *Ztschr. phys. Chem.*, 26, 133.

II. The Proteids of the Wheat Embryo.

THE AQUEOUS EXTRACT.

The germ flour, described on page 381, when treated with water, yields a gummy mass from which a clear extract is secured with difficulty. From 500 grams of meal an extract was obtained with 2,000 cc. of water, of which 1,400 cc. could be filtered clear. This extract was neutral to litmus, alkaline to lacmoid, and so acid to phenolphthalein that 19 cc. of decinormal alkali were required to neutralize 100 cc. of it to this indicator.

When a freshly prepared, dilute, aqueous extract of the recently ground wheat germs is heated in a water-bath, no coagulation occurs, the solution becoming slightly opalescent. If a more concentrated extract, such as may be obtained by treating 1 part of meal with 5 parts of water is thus heated, the entire solution solidifies to a firm, opaque jelly, free from visible particles. If to either of these solutions a very little hydrochloric acid is added before heating, an abundant flocculent coagulum separates on heating.

After standing awhile, the aqueous extract becomes gradually acid to litmus, so that when heated slowly it becomes turbid at about 50° and a large flocculent coagulum separates at 55°. Heated to 65° for some time and filtered, a second coagulum may be obtained on raising the heat from 65° to 100°. The amount of this second coagulum is about one-third that of the first.

The coagulated proteid is dissolved by 0.5 per cent. potassium hydroxide solution, but not perceptibly by 0.4 per cent. hydrochloric acid solution, unless the latter is heated, when a clear transparent jelly is formed.

Freed from coagulable protein, the aqueous extract still contains a relatively large amount of substance which has the reactions of proteose.

When the concentrated aqueous extract is poured into a large volume of distilled water, a turbidity forms at first, which mostly disappears after shaking, indicating the absence of a notable quantity of globulin held in solution by the salts dissolved from the meal.

Saturation of the extracts with sodium chloride gives a considerable precipitate, only a small part of which can be redis-

solved in dilute salt solution. When this dissolved part is precipitated by again saturating with salt, it also is converted, to a large extent, into an insoluble form; the part still remaining in solution is, like a globulin, precipitated by dialysis.

When the solution saturated with sodium chloride is filtered, and the diluted filtrate saturated with ammonium sulphate, a part of the precipitate produced, when redissolved in water, is thrown out of solution by saturating with sodium chloride, though before precipitation with ammonium sulphate it dissolved in saturated sodium chloride solution.

These reactions show that changes occur which involve the albumin coagulating at 55° , for after freeing the extract from all protein precipitable by saturating with salt or by dialysis, there remains in solution only a small proportion of this albumin.

Thus, an aqueous extract corresponding to 666 grams of germ meal, when heated to 65° , yielded 62 grams of coagulum, or 9.3 per cent.; a similar extract on dialysis deposited 9.2 per cent., only 0.87 per cent. of coagulable and 2.0 per cent. of uncoagulable protein remaining in solution. The precipitate, produced by dialysis, was but slightly soluble in salt solution, having become largely coagulated. From these facts it is clear that one and the same protein substance gives rise to these apparently different protein bodies, and consequently the substance which O'Brien considered to be a globulin of the myosin type and an albumin, coagulating at 80° , are in fact derivatives of the same protein substance.

The cause of these changes was not determined, though it seems most probable that they are the result of a slow development of acid in the extract, which, by uniting to the protein in increasing proportions, forms chemically different substances. Such a development of acid takes place rapidly in muscle plasma, under the influence of which quite similar changes in the proteins there present can be observed.

Why Frankfurt overlooked albumin, present in such large proportion in the aqueous extract, is not easily understood, unless, before heating his solutions, he either added no acid or too much, so that he converted this substance into an uncoagulable acid compound.

Hydrochloric acid added to the extract in very small quantity

causes a flocculent coagulum to separate on heating, while a slightly larger quantity, added before heating, entirely prevents the formation of this coagulum. Acetic acid and nitric acid give precipitates in the extracts which are not soluble in a reasonable excess of either of these acids.

In order to determine definitely the relations of these variously obtained substances, we have made a large number of fractional precipitations under quite different conditions, an account of which we now give:

An extract was made by treating 700 grams of germ meal with seven times its weight of water, straining through bolting-cloth and filtering the liquid perfectly clear. This was slightly colored, perfectly neutral to litmus, alkaline to lacmoid, and strongly acid to phenolphthalein. A portion of it was at once heated for one hour in a water-bath at 60°, and the large coagulum produced was filtered out, washed thoroughly with hot water and with alcohol and dried over sulphuric acid, giving 24 grams of preparation 1.

Another preparation was made by heating in a water-bath at 65°, 2,000 cc. of a clear aqueous extract, obtained by treating 3,000 grams of the germ meal with 9,000 cc. of water. The coagulum produced, when washed with hot water and alcohol and dried over sulphuric acid, weighed 62 grams, forming more than 9 per cent. of the oil-free germ meal. This is preparation 2.

Another aqueous extract was heated at 65°, until all the proteid coagulable at this temperature had separated. The coagulum produced, when washed with hot water and alcohol was dried over sulphuric acid and found to weigh 16.68 grams. The filtrate from this coagulum, heated in a boiling water-bath, yielded a second coagulum which, when washed and dried, formed preparation 3, weighing 4.9 grams.

A portion of the extract, which yielded preparation 1, was saturated with ammonium sulphate; the resulting precipitate was dissolved as far as possible in water, its solution filtered clear, and dialyzed for four days. During this time a considerable precipitate formed, that, when filtered out, was found to be insoluble in salt solution. The solution, filtered from that substance and dialyzed in running water until nothing more sepa-

rated, was filtered and heated at 60°, which caused a coagulum. This coagulum, washed with hot water and with alcohol and dried over sulphuric acid, weighed 7.1 grams and made preparation 4.

In a clear water extract of wheat germ meal, dialyzed four days, there appeared a dense turbidity, due apparently to a globulin, since it dissolved on adding sodium chloride. Passing carbon dioxide gas through the dialyzing solution seemed to increase the turbidity, but effected no definite separation. As it was found that 10 cc. of N/10 hydrochloric acid per 100 cc. of the extract caused a separable precipitate, this proportion was added and the resulting flocculent precipitate brought into solution again by adding salt. The clear extract was then dialyzed for two days in running water and filtered from an amorphous precipitate, which was treated as later described on p. 400.

The filtrate from this precipitate was further dialyzed for three days more in running water and then, as nothing separated, for four days more into alcohol. The precipitate which resulted was dried over sulphuric acid, exhausted with water, in order to remove all uncoagulated proteids, as well as other soluble substances, dehydrated with absolute alcohol, again dried and weighed, yielding 12 grams of preparation 5.

Another aqueous extract was saturated with pure sodium chloride, the abundant precipitate filtered out, treated with dilute brine and the resulting solution filtered from a relatively considerable quantity of insoluble matter. This filtrate was saturated with sodium chloride, a second precipitate filtered out and likewise treated with dilute salt solution. The insoluble portion was removed by filtration and the clear filtrate dialyzed. The small precipitate separated by dialysis was washed and dried, weighed 4.8 grams, and formed preparation 6.

The filtrate from the first precipitation of the substance of preparation 6, caused by saturating its solution with sodium chloride, as described above, was diluted with water and saturated with ammonium sulphate. The precipitate which resulted was dissolved in water and its solution precipitated by saturating with sodium chloride. Although this substance had previously been soluble in saturated brine, after precipitation with ammonium sulphate it was found to be nearly all insoluble

therein, so that almost complete precipitation resulted on again saturating with sodium chloride. The precipitate so produced was filtered out, dissolved in dilute salt solution, and reprecipitated by dialysis. We thus secured 7.6 grams of preparation 7.

By saturating another aqueous extract of germ meal with sodium chloride a very large quantity of proteid was separated which was filtered out, exhausted with dilute salt solution and washed thoroughly with water and alcohol. Dried over sulphuric acid, the preparation, 8, weighed 17 grams.

The filtrate and saline washings from preparation 8 were united and again saturated with salt, and yielded a small precipitate which, dissolved in brine and precipitated by dialysis, gave preparation 9, weighing 2.8 grams. As the salt-saturated solution from which this preparation had separated contained so little protein, it appears that nearly all the proteid precipitated from the aqueous extract by saturating with salt had been converted into the insoluble substance forming preparation 8.

The filtrate, from the salt-saturation precipitate produced in the aqueous extract, was dialyzed in water for several days and the still clear solution then dialyzed in alcohol for twenty-four hours. The proteid, thereby precipitated in a coagulated state, was filtered out, washed with water and then with alcohol, yielding 12.4 grams of preparation 10.

Another aqueous extract was saturated with sodium chloride and the precipitate, treated in the same way as preparation 8, yielded 18 grams of preparation 11.

The saline washings of the last preparation were dialyzed free from chlorides and gave a precipitate weighing 2.86 grams when washed and dried, which formed preparation 12, having the properties of a globulin, dissolving readily on adding salt and being precipitated from such solution by water.

The filtrate from the final precipitation of 12, when heated in a boiling water-bath, gave a coagulum which formed preparation 13, weighing 1.64 grams.

The salt-saturated filtrate from the first precipitation of 11, as already described, was heated to boiling and the coagulum produced was filtered out, giving preparation 14, weighing 5.47 grams.

Since analysis showed that most of the preparations already

described contained phosphorus, some even in large amount, we made an attempt to separate the phosphorus from our extract, in order to determine, if possible, the relation of the preparations free from phosphorus to those which contained much phosphorus.

Two thousand grams of meal were treated with 6 liters of distilled water and the extract (4 liters) was squeezed out as completely as possible in a press.

As a preliminary experiment, 100 cc. of this clear, filtered extract were made faintly alkaline to phenolphthalein, with about 40 cc. of N/10 potassium hydroxide solution. To insure a sufficient quantity, 20 cc. more of alkali were added and thereupon a little calcium chloride, which gave a precipitate that seemed to partly dissolve on adding sodium chloride. The undissolved part, when washed with dilute salt solution, water, and alcohol and dried, weighed 1.7 per cent. of the meal, contained about 55 per cent. of organic matter, and left 45 per cent. of ash, consisting of tricalcium phosphate.

To 2,000 cc. of the original extract were then added 1,350 cc. of a solution containing alkali equivalent to 1,560 cc. N/10 solution, with sodium chloride enough to form 6.5 per cent. of the total liquid. To this, a solution of calcium chloride was added, as long as a precipitate formed, and after standing over night the solution was decanted from the precipitate and filtered clear on a pulp filter. Of the clear filtrate, 2,200 cc. were made as neutral as possible to *litmus*, by adding 180 cc. of N/10 hydrochloric acid solution. Of the thus neutralized solution, 1,000 cc., when gradually heated in a water-bath, became turbid at 52° and a considerable coagulum separated at 53°. After the temperature had been slowly raised to 65° and kept at this point for some time, the coagulum was filtered out, washed and dried as usual, giving preparation 15, weighing 6.4 grams. Another portion of this extract, filtered from the calcium chloride precipitate, was saturated with ammonium sulphate while still slightly alkaline to litmus, the resulting precipitate filtered out, dissolved in water, its solution filtered clear and dialyzed. A slight precipitate formed on dialysis, which was removed by filtering, the solution was heated in a boiling water-bath and the proteid thus coagulated was filtered out, washed, dried, and weighed as usual, giving 3.07 grams of preparation 17.

To determine what effect the removal of the phosphorized substance thrown out by calcium chloride had upon precipitation with salt, we made neutral to litmus a liter of the filtrate from the calcium chloride precipitate and then saturated with sodium chloride. The large precipitate which formed was washed by decantation with water, in which it gradually dissolved, until only an insignificant quantity remained. The similarly obtained precipitate from the simple aqueous extract we have shown on page 389, to be nearly all insoluble in water.

To separate globulin from the aqueous extract, 1,200 cc. of clear, filtered extract were obtained from 200 grams of the germ meal treated with 2,000 cc. of water. One liter of this extract was dialyzed in running water for six days, and the large precipitate resulting filtered out, washed with water and alcohol, and dried over sulphuric acid, giving preparation 18, weighing 9.17 grams.

These preparations, thus variously obtained from the aqueous extract, were dried to constant weight at 110° and analyzed with the following results, most of the figures given in the table being the average of closely agreeing duplicate determinations:

TABLE I.—COMPOSITION OF PREPARATIONS OF PROTEID FROM THE WATER EXTRACT OF THE WHEAT EMBRYO.

	1	2	3	4	5	6	7	8	9
Carbon.....	51.13	50.52	50.17	52.39	51.77	52.13	52.73	43.59	52.28
Hydrogen..	6.85	6.81	7.01	6.83	6.81	7.04	7.11	5.77	6.97
Nitrogen...	16.28	16.47	16.66	16.20	16.11	16.48	16.00	15.16	16.38
Sulphur....	1.18	1.17	1.00	1.32	1.30	1.49	1.53	0.90	1.39
Phosphorus	0.72	0.97	0.91	trace	0.17	0.06	none	3.38	0.07
Ash.....	2.73	2.90	3.03	0.35	1.39	0.43	0.39	13.04	0.44
P ₂ O ₅ in ash	1.88	2.09	1.91	trace	0.47	trace	none	6.73	trace
	10	11	12	13	14	15	16	17	18
Carbon.....	51.21	46.67	51.87	51.95	51.65	52.02	49.59
Hydrogen..	6.85	6.19	6.89	6.86	6.66	7.00	6.68
Nitrogen...	16.18	15.89	16.65	16.31	16.08	16.02	16.09	16.45	16.34
Sulphur....	1.10	0.93	1.19	1.35	1.60	1.13	1.12	1.24	0.91
Phosphorus	0.46	2.53	trace	trace	trace	trace	trace	none	1.85
Ash.....	2.19	8.17	0.38	0.45	0.32	1.09	2.83	0.56	2.50
P ₂ O ₅ in ash	1.11	5.71	trace	trace	trace	trace	trace	none	1.79

Assuming that those of the foregoing preparations which contain phosphorus are compounds of protein with the nucleic acid,

which was separated from the aqueous extract of wheat germs and the composition of which is given on page 383 of this paper, and also assuming that all the phosphorus of these preparations is a part of the nucleic acid, we have calculated the composition of these preparations free from nucleic acid. The analyses were further calculated ash-free by subtracting the phosphorus pentoxide contained in the ash from the total ash, which seems permissible since the ash consisted almost wholly of metaphosphates of potassium and sodium, strongly indicating that the phosphorus pentoxide was derived from the nucleic acid. These calculations gave the following results:

TABLE II.—COMPOSITION OF LEUCOSIN CONTAINED IN THE PREPARATIONS FROM WATER EXTRACTS OF THE WHEAT EMBRYO.

	1	2	3	4	5	6	7	8	9
Carbon	52.93	52.75	52.41	52.57	52.57	52.47	52.93	53.23	52.64
Hydrogen..	7.12	7.16	7.38	6.85	6.91	7.08	7.13	7.09	7.02
Nitrogen...	16.45	16.68	16.94	16.26	16.27	16.55	16.06	16.30	16.46
Sulphur ...	1.29	1.32	1.13	1.32	1.34	1.50	1.53	1.60	1.41
Oxygen....	22.21	22.09	22.14	23.00	22.91	22.40	22.35	21.78	22.47
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	10	11	12	13	14	15	16	17	18
Carbon	52.63	52.44	52.06	52.11	52.16	52.30	53.45
Hydrogen..	7.06	7.10	6.92	6.88	6.73	7.04	7.30
Nitrogen...	16.40	16.26	16.71	16.38	16.13	16.20	16.56	16.54	16.57
Sulphur....	1.17	1.34	1.19	1.35	1.60	1.14	1.15	1.24	1.16
Oxygen	22.74	22.86	23.12	23.28	23.77	22.88	21.52
	100.00	100.00	100.00		100.00	100.00		100.00	100.00

Of these, preparation 1, 2, 3, 4, 13, 14, 15, 16, and 17 were obtained by coagulation with heat, 5 and 10 by coagulation with alcohol, 8 and 11 by saturation with sodium chloride, 6, 7, 9, and 12 by dialyzing salt solutions in water, and 18 by direct dialysis of the aqueous extract. Since some of these preparations formed the whole of the precipitable proteid contained in the extract, while others represented fractions, it is evident that all contain one and the same protein substance mostly combined with various proportions of nucleic acid.

Eliminating the nucleic acid, it thus appears that the composition of the protein part of those preparations which contain phosphorus is the same as that of the phosphorus-free proteid

preparations, although the former contain from very little up to more than 37 per cent. of nucleic acid.

Most of these preparations might, in accordance with custom, be called nucleoproteids, while 8 and 11 are, both in properties and composition, very much like nuclein. It is thus evident that these nucleoproteids and nucleins are nucleic acid compounds of protein which, owing to the high molecular weight of the nucleic acid, are more readily recognized as compounds than are those with acids of low molecular weight.

It is to be noted that these preparations show very diverse properties: some being like albumin; some like globulin; some being precipitated by saturation with salt, while others are not. As we have shown, these different properties are the result of changes caused by varying the conditions under which the proteid exists in the extract, and depend chiefly on the degree of acidity of the extract, whereby the numbers and kinds of acid molecules that combine with the protein molecule are altered.

Whatever may be the true cause of these changes, it is evident from the results here described, that the distinctions heretofore made between globulin and albumin, myosin and vitellin, etc., have very little value as a basis for classifying protein substances. This explains the difference between O'Brien's classification of leucosin as a myosin-like globulin, to which reference was made at the beginning of this paper, and our designation of it as an albumin, because of the ready solubility in water and coagulability by heat of the preparations which we had made.

Thus, preparation 18, weighing 9.17 grams, was insoluble in water and in salt solution and was not a precipitate of globulin, since in the filtrate from which it had separated on dialysis, only 0.87 gram of coagulable albumin was found instead of 9.5 grams as usually found by direct coagulation of the aqueous extracts; moreover the analysis shows it to be a compound of leucosin with 20 per cent. of nucleic acid.

On the preceding pages, it was shown that a small part of the precipitate, produced by saturating the aqueous extract with sodium chloride, is soluble in dilute salt solution and can be precipitated from this solution by dialysis, as a globulin-like substance, readily soluble again in salt solution. The precipitates thus obtained contain little or no nucleic acid, and have

very nearly the same elementary composition as leucosin, of which they are evidently compounds with a small proportion of some body of low molecular weight.

It is plain from these facts that O'Brien's myosin contains the same protein substance as my leucosin.

O'Brien's "*albumin*" coagulating at 75°-80° is unquestionably more of this same leucosin as shown by preparation 3, which formed about 25 per cent. of the total coagulable proteid. It has been the writer's experience that complete coagulation, especially in a solution quite free from salts, can be effected, if at all, only by heating the solution much above the lower coagulation temperature of the proteid to be separated.

From the whole seed we obtained leucosin with the same composition and general properties as from the embryo, but our preparations from the whole seed were free from phosphorus. This was probably because the proportion of nucleic acid to protein matter was smaller in the whole seed than in the embryo so that on extracting with water the nucleic acid did not form soluble compounds with the leucosin, but remained undissolved in combination with protein. In the following table is given the average of analyses of leucosin from the cereals.

TABLE III.—COMPOSITION OF LEUCOSIN PREPARED FROM VARIOUS CEREALS.

	Wheat embryo.	Wheat kernel.	Rye kernel.	Barley kernel.	Barley malt.	Maize ¹ kernel.
Carbon	52.65	53.02	52.97	52.81	53.07	52.72
Hydrogen....	7.04	6.84	6.79	6.78	6.72	7.05
Nitrogen	16.43	16.80	16.66	16.62	16.71	16.82
Sulphur	1.32	1.28	1.35	1.47	} 23.50	1.32
Oxygen.....	22.56	22.06	22.23	22.32		22.05
	100.00	100.00	100.00	100.00	100.00	100.00

In an earlier paper on the "Chemical Nature of Diastase"² we pointed out that diastatic action appeared to be always associated with leucosin. Since our extracts of wheat embryo were so rich in leucosin, we determined the diastatic power of the

¹ This proteid was described by Chittenden and Osborne (*Am. Chem. J.*, 13, 327) as a myosin-like globulin, and was later (*This Journal*, 19, 535) designated *maysin* by the writer. Since we now find that leucosin may form compounds having the properties of globulin, it is probable that *maysin* and leucosin contain one and the same protein substance.

² *This Journal*, 18, 542; Report Conn. Agr. Exp. Sta., 1895, p. 239.

germ meal by extracting with four times its weight of water and found that, under the conditions of Lintner's test, 0.10 cc. of the extract so made, when added to 10 cc. of a 2 per cent. solution of soluble starch, formed within one hour, at 20°, enough sugar to reduce 5 cc. of Fehling's solution. The 0.10 cc. of extract corresponds to 25 milligrams of the germs, from which it is seen that this meal possesses high diastatic power, though it is inferior in this respect to active malt.

SODIUM CHLORIDE EXTRACT.

Wheat germ meal treated with 10 per cent. sodium chloride brine forms a dense jelly-like mass from which it is nearly impossible to separate the solution.

With 3 per cent. brine a manageable extract can be made by using from six to ten times as much solvent as meal. Thus, 100 grams of the meal treated with 600 cc. of 3 per cent. salt solution yielded in fifteen hours 400 cc. of clear filtrate. As has just been shown, the aqueous extract on dialysis, in consequence of a change which affects leucosin, deposits a large amount of proteid, chiefly in the coagulated form. In order to obtain preparations of the proteid substance soluble in salt solutions, but insoluble in water, which should be free from this coagulable albumin, we treated 2,000 grams of germ meal with 20 liters of 3 per cent. salt solution heated to 70°, whereby the leucosin was coagulated and the salt-soluble globulin brought into solution. The extract, neutral to litmus, was filtered clear, at once saturated with ammonium sulphate and the proteids thus precipitated collected on a filter, dissolved in water, and the clear solution dialyzed in running water.

Proteid matter separated on dialysis in spheroids which, like legumin, conglutin, and amandin, united to a plastic mass on the bottom of the dialyzer.

This precipitate was dissolved in brine, filtered absolutely clear, dialyzed for 48 hours, the large precipitate which separated allowed to settle, and the solution, which was nearly free from protein, decanted.

A portion of the precipitate was washed first with water, which rendered it opaque and dense, then with dilute and finally with absolute alcohol and dried over sulphuric acid. This weighed

5.22 grams, and is preparation 19. The rest of the precipitate was completely dissolved in 125 cc. of 10 per cent. salt solution. To this, water was added until its volume was 425 cc., thus making a salt solution of nearly 3 per cent. From this diluted solution a gummy deposit separated from which the liquid was soon completely decanted. The latter was further diluted with 325 cc. of water and the precipitate which resulted allowed to settle to a viscid transparent deposit. From this precipitate the solution was again decanted and dialyzed for 48 hours, but not more than a trace of globulin was deposited. The two precipitates produced by dilution were thoroughly washed with water and alcohol, dried over sulphuric acid and formed preparations 20 and 21, weighing respectively 11.4 grams and 8.15 grams. A part of each of these preparations was set aside for analysis and the rest, dissolved together in 10 per cent. salt solution, allowed to stand over night at 4°. The solution was then decanted from a slight sediment, filtered clear and heated to 80° in order to coagulate any leucosin which might be present, and after two hours filtered from a very small coagulum which had gradually formed.

This filtrate was dialyzed in water for four days and the globulin which separated was washed with water and with alcohol and dried over sulphuric acid, giving preparation 22.

The solution filtered from the first dialysis precipitates which yielded preparations 19, 20, and 21; was further dialyzed; a little globulin, which separated, was filtered out and the filtrate dialyzed into alcohol for four days. A precipitate was produced which, when washed with absolute alcohol and dried, weighed 25 grams. This substance consisted of proteid which will be described later, on page 402. Another series of fractional precipitations of this globulin-like proteid was made by extracting four kilograms of the oil-free germ meal with 27 liters 3 per cent. brine, heated to 67° at the time it was applied to the meal. The mixture was thoroughly stirred and thrown on filters. A clear filtrate of about 12 liters was finally obtained, which was saturated with ammonium sulphate. The precipitate produced was dissolved in water and its solution dialyzed for forty-eight hours, whereupon a large quantity of spheroids separated which on settling united to a coherent mass. This pre-

precipitate was washed by decantation with water, dissolved in brine, and its solution made faintly alkaline to litmus by cautiously adding N/10 potassium hydroxide solution. In order to separate phosphoric acid, a little calcium chloride solution was then added to this very slightly alkaline liquid and the latter, though apparently free from any precipitate of calcium phosphate, was filtered, whereby a little suspended matter was removed. The solution was made exactly neutral to litmus by adding 56 cc. N/10 hydrochloric acid and dialyzed for eighteen hours. A gummy precipitate, A, adhering to the bottom of the dialyzer, then separated, from which the solution, B, was decanted almost completely.

The precipitate, A, was dissolved in about 200 cc. of 5 per cent. brine and the liquid was poured into 800 cc. of water. The resulting flocculent precipitate settled rapidly to a coherent deposit from which the solution was decanted. The deposit was repeatedly washed by decantation with water, which caused it to lose its gummy character and become opaque, white, and granular. After dehydrating with absolute alcohol and drying over sulphuric acid it weighed 15.5 grams and was marked preparation 23. The solution marked B was further dialyzed for forty-eight hours when a second precipitate formed, which, like 23, completely dissolved in brine, to a solution perfectly neutral to litmus. This precipitate was washed by decantation with water, but the finer part settled so slowly that it was necessary to decant it together with the water. The sediment after exhausting with absolute alcohol and drying, weighed 23.5 grams, and formed preparation 24. On long standing, the decanted washings deposited the finely divided matter, which was then collected on a filter, dissolved in brine and its solution precipitated by water, giving 15.4 grams of preparation 25.

To determine the quantity of globulin contained in our oil-free germ meal, we treated 200 grams of the meal with 2,000 cc. of 3 per cent. salt solution heated to 65° and filtered the extract perfectly clear. Of this, 1,000 cc. were dialyzed until free from chlorides, when the precipitate of spheroids was filtered out, washed with water and with alcohol and dried over sulphuric acid. This preparation, 26, formed 5.05 per cent. of the oil-free meal.

To obtain a quantity of this globulin for digestion with pepsin, a quantity of germ meal was extracted with 3 per cent. salt solution heated to 70°, the extract was filtered clear and saturated with ammonium sulphate. The precipitate produced was dissolved in water and the resulting gummy and somewhat turbid solution filtered clear. The filtrate was dialyzed until the solution gave no turbidity on pouring into distilled water. The proteid, which had then separated in spheroids, was filtered out, washed by decantation with water and with alcohol and dried over sulphuric acid, giving 27.3 grams of preparation 27.

A part of the extract from which 27 had been prepared was mixed with an equal volume of N/10 potassium hydroxide, about twice the quantity necessary to neutralize the extract to phenolphthalein. The solution was then dialyzed in distilled water frequently renewed and in this way a considerable quantity of phosphorus was separated in the alkaline dialyzate. When all, or nearly all, which it was possible to separate in this way, had been removed, the solution in the dialyzer was neutralized with N/10 hydrochloric acid until it no longer reacted alkaline to litmus. This caused a turbidity. The acid was then further added until an acid reaction with litmus was obtained, producing a precipitate from which, after settling, the solution was decanted. The precipitate was then dissolved in brine, its solution filtered clear and dialyzed, whereby a substance was precipitated in spheroids, which was filtered out, washed with water and alcohol and formed preparation 28, weighing 3 grams.

These preparations had the following composition :

TABLE IV.—COMPOSITION OF PREPARATIONS EXTRACTED BY SODIUM CHLORIDE SOLUTIONS FROM THE WHEAT EMBRYO.

	19	20	21	22	23	24	25	26	27	28
Carbon	48.77	50.03	50.23	48.17	49.39	48.75	49.79	48.67
Hydrogen	6.44	7.04	6.89	6.54	6.78	6.52	6.76	6.56
Nitrogen ...	18.14	18.21	18.12	18.39	18.23	18.06	17.95	18.16	18.01	17.97
Sulphur	0.49	0.56	0.51	0.60	0.53	0.55	0.48	0.63	0.61	0.61
Phosphorus	1.15	1.03	1.35	0.76	0.56	1.41	1.17	1.41	1.11	1.55
Ash	2.29	1.86	2.25	1.30	1.22	3.85	2.60	2.66	1.11	2.94
P ₂ O ₅ in ash.	1.66	1.34	1.68	0.84	0.80	2.00	1.82	2.00	0.68	2.30

These analyses, when calculated free from nucleic acid and ash, as was done for the albumin preparations, in the manner described on page 392, gave the following results :

TABLE V.—COMPOSITION OF THE GLOBULIN CONTAINED IN THE PREPARATIONS EXTRACTED FROM THE WHEAT EMBRYO BY SODIUM CHLORIDE SOLUTION.

	19	20	21	22	23
Carbon	51.37	51.58	51.40
Hydrogen	6.83	7.31	7.08
Nitrogen	18.59	18.59	18.62	18.70	18.45
Sulphur	0.57	0.63	0.60	0.66	0.57
Oxygen	22.58	21.75	22.50
			100.00	100.00	100.00
	24	25	26	27	28
Carbon	51.56	51.86	51.40	51.98	51.70
Hydrogen	7.07	7.19	6.94	7.12	7.05
Nitrogen	18.85	18.41	18.71	18.37	18.53
Sulphur	0.67	0.55	0.75	0.70	0.75
Oxygen	21.85	21.99	22.20	21.83	21.97
	100.00	100.00	100.00	100.00	100.00

These figures plainly show that our globulin preparations are mixtures of nucleates of one and the same protein substance and contain from 5 to 15 per cent. of nucleic acid. The preparations contain the same protein as the globulin which one of us has previously described as occurring in the kernel of wheat, rye, barley, and maize. In the entire kernel, so little of this globulin is present that it is difficult to prepare it pure therefrom. For this reason, we think, the analyses given below do not agree as closely as they might otherwise be expected to. From the whole seed this globulin is obtained entirely free from phosphorus, which we attribute to the much greater proportion of proteid matter to nucleic acid, in the seed, compared with that existing in the wheat embryo.

TABLE VI.—COMPOSITION OF THE GLOBULIN CONTAINED IN VARIOUS CEREALS.

	Wheat embryo.	Wheat ¹ kernel.	Rye ² kernel.	Maize ³ kernel.	Barley ⁴ kernel.
Carbon	51.57	51.03	51.19	51.99	50.88
Hydrogen	7.07	6.85	6.74	6.81	6.65
Nitrogen	18.60	18.39	18.19	18.02	18.10
Sulphur	0.65	0.65	23.88	0.66	24.37
Oxygen	22.11	23.08		22.52	
	100.00	100.00	100.00	100.00	100.00

¹ *Am. Chem. J.*, 15, 392.² *This Journal*, 17, 429; also Report of Conn. Expt. Station for 1894, p. 147.³ *Am. Chem. J.*, 13, 327, 385 and 15, 20.⁴ *This Journal*, 17, 539; also Report of Conn. Expt. Station for 1894, p. 165.

Having determined the composition of this globulin-like proteid and also that of the albumin, it became clear that several preparations obtained from the aqueous extract were mixtures of these two substances, thus showing the globulin to be present to some extent in the aqueous extract.

As noted on page 388, when 2,000 cc. of an aqueous extract of about 650 grams of the meal were dialyzed in running water for four days, a dense turbidity was formed which could not be removed by filtration. This, however, on adding a little hydrochloric acid, was converted into a precipitate, which was readily dissolved by adding sodium chloride sufficient to make a 3 per cent. solution, and was precipitated from this solution by dialysis. We thus obtained 9 grams of preparation 29, which, dried at 110° , had the following composition :

COMPOSITION OF PREPARATION 29.

	I.	II.	Av.	Corrected for ash and nucleic acid.	Calculated for 60 per cent. globulin, 40 per cent. leuco- sin.
Carbon	48.30	47.92	48.11	51.70	51.95
Hydrogen	6.49	6.41	6.45	7.07	7.07
Nitrogen	17.40	17.24	17.32	17.74	17.74
Sulphur	0.83	0.85	0.84	1.08	0.91
Phosphorus	1.91	1.91
Oxygen	22.51	22.53
Ash	3.95				
P ₂ O ₅ in ash	2.95			100.00	100.00

This analysis corresponds pretty nearly with that of a mixture of 60 per cent. of the globulin with 40 per cent. of leucosin, except that the amount of sulphur found was somewhat greater than that calculated.

After heating another portion of the same aqueous extract to 65° for some time and filtering off the coagulum, the filtrate was dialyzed for five days into alcohol and the precipitate thereby produced filtered out and exhausted with water. The residue of proteid matter coagulated by alcohol, weighing 6.7 grams and marked preparation 30, was then dried at 110° and analyzed with the following results :

COMPOSITION OF PREPARATION 30.

		Corrected for ash and nucleic acid.	Calculated for globulin 40 per cent., leucosin 60 per cent.
Carbon.....	49.49	51.80	52.13
Hydrogen	6.81	7.14	7.03
Nitrogen.....	16.87	17.32	17.30
Sulphur	0.93	1.14	1.05
Phosphorus	0.89
Oxygen	22.60	22.49
Ash.....	4.00
P ₂ O ₅ in ash.....	2.01	100.00	100.00

This analysis corresponds quite nearly with that of a mixture of 40 per cent. of the globulin with 60 per cent. of the albumin.

THE PROTEOSE OF THE WHEAT EMBRYO.

In making the preparations already described considerable quantities of crude proteose were obtained from both the aqueous and sodium chloride extracts. After the 'leucosin and the globulin had been separated as completely as possible, the solutions containing the proteoses, as well as the unseparated residues of other proteids, were dialyzed into alcohol and the precipitates produced washed and dried over sulphuric acid.

A mixture, weighing 15.4 grams, was made by uniting several such preparations that had been obtained from aqueous extracts from which most of the other proteids had been separated, without heat, by saturating with sodium chloride and dialysis into alcohol. The mixture contained much matter made insoluble in water by the final treatment with alcohol. This was filtered out, washed thoroughly with water and with alcohol and when dried weighed 4.18 grams, and was marked preparation 31. The filtrate from this was saturated with ammonium sulphate, the precipitate redissolved and again precipitated in the same way. The solution of the second precipitate was dialyzed in cold distilled water until free from sulphate, and then for several days in alcohol. The precipitate thus produced was dissolved in water, a little insoluble matter filtered out, and its clear solution saturated with sodium chloride, which produced a small precipitate. This was filtered out, dissolved, and its solution dialyzed in water. The salt-saturated filtrate was likewise dialyzed and when both solutions were free from chlorine the dialyzers were

transferred to alcohol and the proteose thereby precipitated. The proteose separating on saturation with salt, gave 0.6 gram of preparation 32; that from the salt-saturated solution, 0.97 gram of preparation 33. This small yield of proteose indicates great impurity of the original crude product and shows that the proportion of proteose to other proteids is very small.

Another crude product was obtained by dialyzing into alcohol an aqueous extract, after separating leucosin which had been coagulated by heat. This, weighing 35 grams, was dissolved in water and the insoluble matter filtered out, washed and dried, giving preparation 34, weighing 7.26 grams.

The filtered solution was saturated with ammonium sulphate, the precipitate dissolved in water, and the clear solution dialyzed in distilled water until free from sulphates, and then in alcohol. The substance thus separated was again dissolved in water, and its solution saturated with salt; the precipitate thus produced was dissolved in water and its solution, as well as the salt-saturated filtrate, were dialyzed in water. When free from chlorine, these solutions were dialyzed in alcohol and yielded, respectively, preparations 35, weighing 4 grams and 36, weighing 1.84 grams.

Another preparation of crude proteose was obtained by extracting the meal with 3 per cent. sodium chloride solution heated to 70°, dialyzing the extract in water, coagulating the leucosin by heat and precipitating the proteose by dialysis in alcohol. A mixture of such preparations, weighing 31.6 grams, was treated with water, the insoluble matter filtered out, washed and dried, giving 5.16 grams of preparation 37.

The filtered solution was saturated with ammonium sulphate, the precipitate dissolved in water, the solution dialyzed in distilled water till free from sulphate, and then in alcohol. The separated proteose was redissolved in water and its solution saturated with sodium chloride. The precipitate which resulted was filtered out, dissolved in water and its solution, as well as the salt-saturated filtrate, was dialyzed in water till free from chlorine, and finally in alcohol.

The products thus obtained, formed, respectively, preparations 38, weighing 0.75 gram and 39, weighing 1.35 grams. One other proteose preparation was made from the aqueous

extract previously described on page 390 from which the phosphorus was largely separated by making it slightly alkaline and adding calcium chloride. After heating the extract to boiling and filtering out the coagulum, the filtrate was dialyzed into alcohol, the resulting precipitate dehydrated with absolute alcohol, dried over sulphuric acid, redissolved in water, and precipitated by saturating with ammonium sulphate. The gummy precipitate, having the general appearance and properties of similar precipitates of the proteoses obtained by the action of pepsin, was dissolved in water, dialyzed free from sulphates, and then precipitated by dialysis in alcohol, giving 2 grams of preparation 40.

These preparations were dried at 110° and analyzed with the following results:

TABLE VII.—COMPOSITION OF ALCOHOL-COAGULA AND OF PROTEOSE PREPARED FROM THE WHEAT EMBRYO.

	Residues of other proteids coagulated by alcohol.			Proteose precipitated by sodium chloride.			Proteose soluble in saturated NaCl sol.			
	31	34	37	32	35	38	33	36	39	40
Carbon ...	52.36	49.44	51.93	49.94	48.46	48.70	48.44	48.99
Hydrogen..	6.98	6.85	6.87	6.80	6.70	6.73	6.71	6.85
Nitrogen..	16.01	16.00	16.30	16.79	17.08	16.26	16.91	16.76	16.16	16.89
Sulphur ..	1.85	4.08	1.30	1.24	27.93	27.81	28.69	1.10
Oxygen ...	22.80	23.63	23.60	24.94				
	100.00	100.00	100.00		100.00		100.00	100.00	100.00	100.00
Ash	0.81	14.13	0.95		0.30	0.77	1.13	1.00	0.74	1.27

From these analyses it is seen that the matter insoluble in water, forming preparations 31, 34, and 37 consists of coagulated proteid apparently mostly derived from leucosin. The high proportion of sulphur in 31 and 34 is due to calcium sulphate, precipitated by alcohol from the aqueous extract.

The remaining preparations have the low percentage of carbon, characteristic of proteoses made by pepsin digestion.

Whether the proteose precipitated by saturating its solution with salt is a different protein substance from that soluble in saturated salt solution or whether difference in solubility is due to the presence of different acid compounds of one and the same protein substance, is not demonstrated, but the agreement shown by these analyses, considering the difficulty of making quite pure preparations, indicates that the latter is the case.

The Proportions of the Various Proteid Substances of the Wheat Embryo.

Twenty grams of fresh germ meal, from which the ether-soluble constituents had *not* been separated, were treated with 500 cc. of water and after shaking for some time, the extract was filtered clear. Two portions, of 100 cc. each, were treated with a few drops of very dilute hydrochloric acid and heated in a boiling water-bath. The coagulum which separated was collected on a filter and its nitrogen determined. To the filtrate from one coagulum, tannin was added and nitrogen was determined both in the precipitate and in the filtrate. Another lot of 20 grams was treated in the same way and nitrogen determined in the heat-coagulum formed in each of two portions of 100 cc. The amount of nitrogen corresponding to one gram of germ meal was found in the four coagula to be, 0.0163 gram, 0.0156 gram, 0.0159 gram, and 0.0162 gram; in the tannin precipitate 0.0062 gram; and in the solution filtered from the latter 0.0062 gram.

Twenty grams of germ meal were extracted with 500 cc. of 3 per cent. sodium chloride solution heated to 70°, whereby the leucosin was coagulated and the globulin and proteose dissolved. Of the clear filtered extract, 100 cc. yielded with tannin a precipitate containing 0.0166 gram nitrogen per gram of meal extracted.

Two portions of the meal, each of one gram, were exhausted with 3 per cent. sodium chloride solution heated to 70°, and nitrogen determined in the residues. The 0.0331 and 0.0309 gram of nitrogen found in the residues were from the leucosin and insoluble nitrogenous bodies, so that the nitrogen belonging to the latter equaled 0.0171 gram and 0.0149 gram. From the average of these figures we find the following amounts of the different forms of nitrogen in one gram of the wheat germ meal.

	Nitrogen. Gram.
Insoluble in water and salt solution	0.0160
Insoluble in water but soluble in salt solution	0.0100 = globulin nitrogen.
Soluble in water and coagulable by heat	0.0160 = albumin "
Soluble in water, uncoagulable by heat, precipitable by tannin	0.0050 = proteose "
Not precipitable by tannin	0.0060 = non-proteid "
Total	0.0530
Found by direct nitrogen determination	0.0531

We have shown that the coagulated leucosin preparations contain about 10 per cent. of nucleic acid, the globulin about 15 per cent., while those of the proteose contain none. Deducting these quantities from the nitrogen given in the table, we find 9.5 per cent. of the embryo to be leucosin, 4.84 per cent. to be globulin, and 3.03 per cent. to be proteose.

The bodies which are represented by the insoluble nitrogen, we have been unable to separate from the embryo. The residue after extraction with hot salt solution contained 0.0076 gram of phosphorus. Since there was in this residue about 0.1000 gram of coagulated leucosin, in which we have usually found about 1 per cent. of phosphorus, we have 0.0061 gram of phosphorus remaining over. In view of the large proportion of nucleic acid found in the extracts of the embryo, it is not improbable that this phosphorus mostly belongs to nucleic acid, in which case there would be about 6.75 per cent. of nucleic acid containing 0.0108 gram of nitrogen, which leaves only 0.0052 gram of nitrogen for proteid matter in the insoluble residue. It seems probable, therefore, that this insoluble nitrogen largely belongs to compounds of the proteid with relatively much nucleic acid.

DIGESTION OF THE PHOSPHORUS-CONTAINING PROTEIDS WITH PEPSIN-HYDROCHLORIC ACID.

Leucosin Nucleate.—Ten grams of the coagulated albumin, preparation 2, were suspended in 400 cc. of water and dissolved by adding 100 cc. of N/10 potassium hydroxide solution. To the nearly clear solution which resulted, an equal volume of 0.4 per cent. hydrochloric acid was added, together with some pepsin, and the mixture digested at 37°. In a short time the solution became perfectly clear, but later deposited a large coherent precipitate, which gradually contracted, but at the same time retained the form of the lower part of the beaker. From this the clear solution was decanted, the precipitate thoroughly washed by decantation, suspended in water and dissolved by adding 28 cc. of N/10 potassium hydroxide solution, an amount of alkali just sufficient to dissolve all the substance and at the same time make the solution neutral to litmus. When to this solution decinormal acid was gradually added, no precipitate appeared until nearly one-half the quantity of acid required for

complete neutralization had been added, but with 28 cc., the solution was neutralized and also completely precipitated, the addition of 2 cc. more acid giving no turbidity in the solution filtered from the precipitate. This precipitate was washed with water and with alcohol and dried over sulphuric acid, forming preparation 41, weighing 1.54 grams.

To precipitate this substance a quantity of acid was added exceeding that of the alkali employed for solution by just 2 cc. The filtrate from the precipitate, however, required not 2 cc. of alkali, but 8.5 cc. for neutralization to phenolphthalein, showing 6.5 cc. of alkali to have been neutralized by the acid of the nuclein originally dissolved. The neutralized filtrate left, on evaporation, 0.3975 gram of substance, the aqueous solution of which was precipitated by hydrochloric or nitric acid, but *not* by ammonium molybdate solution until after boiling with acid for some little time, when yellow phosphomolybdate was precipitated. These facts indicate the presence in this filtrate of a nucleic acid.

More nuclein was made from the same preparation, 2, by suspending 30 grams in 0.2 per cent. hydrochloric acid, containing pepsin, which, even at 20°, caused within two hours complete solution of the coagulated proteid. The solution was digested at 37° for forty-eight hours, during which time much nuclein separated, having the appearance and properties of the preparation just described.

After decanting the clear solution and thoroughly washing the residual nuclein, the latter was suspended in water and dissolved in 72 cc. N/10 potassium hydroxide. The solution thus obtained was made neutral to litmus by adding 11 cc. of N/10 hydrochloric acid, but no precipitate appeared till 1.5 cc. more of acid were added. To the solution 72 cc. N/10 hydrochloric acid were added, giving a precipitate which, when washed and dried, made preparation 42 and weighed 3.4 grams. The filtrate from this precipitate, as in the former case, was strongly acid, requiring 12 cc. of N/10 potassium hydroxide to neutralize it to phenolphthalein. Two other preparations of nuclein were made from 8.493 grams of 8, and 9.804 grams of 11, both being substances precipitated from the aqueous extract by saturating with sodium chloride. Each portion was suspended in about 300 cc. of 0.2 per cent. hydrochloric acid, containing 0.1 gram of pepsin and,

with frequent stirring, digested at 40° for twenty-four hours. Throughout the digestion a large part of the substance remained undissolved. An equal volume of 0.2 per cent. hydrochloric acid, containing 0.1 gram of pepsin, was again added to each and the digestion continued for twenty-four hours longer. The insoluble matter which remained was not coherent like the two former nuclein products, but consisted of a white, very finely divided substance which was easily filtered out and washed. After dehydrating with absolute alcohol these preparations were dried over sulphuric acid; from 8, 4.04 grams of preparation 43 were obtained and from 11, 4.16 grams of 44.

Globulin Nucleate.—Fifteen grams of a mixture of nearly equal parts of the globulin preparations 23 and 24 were next suspended in 0.2 per cent. hydrochloric acid, containing 0.2 gram of pepsin, which, within a short time, almost completely dissolved the proteid matter. From this solution, on further digestion, the nuclein separated, forming a coherent deposit. After seventy-two hours' digestion, the clear solution was decanted, the deposit dissolved in a little ammonia and its solution filtered perfectly clear from a very slight gelatinous residue. The resulting solution was then treated with acetic acid, added in excess of the amount necessary to neutralize the solution to litmus. Since, even on standing, the precipitate so produced separated imperfectly, an equal volume of alcohol was added. The substance, which then separated well, was filtered out, washed with dilute and with absolute alcohol and dried over sulphuric acid, giving 2.38 grams of preparation 45, or about 16 per cent. of the original substance.

The filtrate from the acetic acid precipitate gave a further slight precipitate on adding hydrochloric acid, which had properties characteristic of nucleic acid.

Still another preparation of nuclein was made from the globulin by suspending 10 grams of 27 in water and adding 50 cc. of N/10 potassium hydroxide. This solution was neutralized and an equal volume of 0.4 per cent. hydrochloric acid at once added, producing a turbid solution, which, however, contained no visible particles. To this, pepsin was added and the mixture digested for forty hours, during which time a coherent deposit of nuclein formed on the bottom of the beaker. From this,

the clear solution was decanted. The deposit was then thoroughly washed with water and dissolved in 43 cc. of N/10 potassium hydroxide. To this clear solution 43 cc. of N/10 hydrochloric acid were added, causing a gummy precipitate which could not be filtered until 15 cc. more acid had been added, when the precipitate rapidly settled as a coherent deposit, from which the solution was soon decanted. This solution required for neutralization to litmus 16 cc. N/10 potassium hydroxide, and to phenolphthalein 18 cc. The precipitate, when washed and dried, gave 2.2 grams of preparation 46.

These six preparations were all dried at 110° and analyzed with the following results:

TABLE VIII.—COMPOSITION OF NUCLEIN FROM THE PROTEIDS OF THE WHEAT EMBRYO.

	41	42	43	44	45	46
Carbon.....	44.87	44.35	42.68	43.35	39.42	41.92
Hydrogen.....	5.82	5.77	5.45	5.47	5.03	5.25
Nitrogen.....	16.04	16.64	16.12	16.01	16.05	17.00
Sulphur.....	0.97	1.03	0.65	0.85	0.53	0.46
Phosphorus...	4.58	5.07	5.32	4.88	5.27	5.63
Ash.....	0.60	0.78	1.72	1.72	17.42	1.17
P ₂ O ₅ in ash....	0.29	0.55	1.24	0.94	10.56	0.69

If we subtract from the total ash the amount of phosphorus pentoxide found in it, we shall have a determination of the bases contained in the ash of these preparations.

We have calculated these analyses of nuclein free from the bases of the ash and from nucleic acid, in the way previously described, with the following results:

TABLE IX.—COMPOSITION OF PROTEIN MATTER CONTAINED IN THE NUCLEIN.

	41	42	43	44	45	46
Carbon.....	53.65	54.77	51.80	52.36	52.30	51.64
Hydrogen.....	7.23	7.46	6.85	6.73	6.91	6.60
Nitrogen.....	16.68	17.56	16.31	16.31	19.31	18.83
Sulphur.....	1.98	2.37	1.61	1.89	1.53	1.25
Oxygen.....	20.46	17.84	23.43	22.71	19.95	21.58
	100.00	100.00	100.00	100.00	100.00	100.00

The composition of the proteid matter in 43 and 44 is very nearly that of leucosin except as regards sulphur, the amount of

which is decidedly greater. On the other hand, 41 and 42, which also were derived from preparations whose protein matter was leucosin, differ in composition very decidedly from that substance. This is probably because on pepsin digestion the substance of preparations 43 and 44 remained throughout undissolved, whereas 41 and 42 separated on pepsin digestion from nearly clear solutions and therefore doubtless their protein matter had been to some degree altered by the pepsin before separating as an insoluble compound with nucleic acid. The two nucleins, 45 and 46, from the globulin which also had separated from solution, show similar differences in composition when compared with the unaltered globulin, carbon and nitrogen being higher and sulphur very much higher than in the globulin. The greatly increased proportion of sulphur would indicate that sulphur in some acid form had split from the proteid molecules undergoing hydrolysis and had become a part of the insoluble nuclein, as did the nucleic acid.

CONCLUSION.

The embryo of the wheat kernel contains:

1. A *nucleic acid* in considerable quantity. This acid is insoluble in water, forms soluble as well as insoluble compounds with proteid substances, and on hydrolysis yields guanin, adenin, phosphoric acid, and other products not yet identified. It has the following composition:

NUCLEIC ACID.

Carbon	36.48
Hydrogen	4.48
Nitrogen	16.17
Phosphorus	8.96
Oxygen	33.91
	<hr/>
	100.00

This acid is not identical with any nucleic acid heretofore described. On hydrolysis it does not yield any form of sugar. From guanylic acid recently described by Bang it also differs distinctly, in that its potash salt is extremely soluble in cold water and the ratio of phosphorus to nitrogen, being 1 to 4 instead of 1 to 5.

2. *Leucosin*, an albumin (yield about 10 per cent. of the

embryo) formerly found by the writer in small quantity in the whole kernel of wheat, rye, and barley, and abundantly in malt. Leucosin begins to separate as a flocculent coagulum when the very slightly acid aqueous extract of the wheat kernel or wheat embryo is heated to 52°. Even after long heating at 65°, the leucosin is only partly separated, and about one-third more coagulum of the same elementary composition is obtained on raising the temperature from 65° to 100°.

By saturating extracts of the kernel or of the embryo with sodium chloride, the leucosin is largely precipitated from the former as a substance readily soluble again in water, from the latter as an insoluble compound containing about 30 per cent. of nucleic acid. From the latter precipitate, dilute salt solution extracts a small amount of nearly phosphorus-free proteid, which behaves like a globulin, being precipitated by dilution or by dialysis, but having essentially the same ultimate composition as leucosin.

By dialyzing the aqueous extract in water, nearly all the leucosin contained in it is precipitated, not like a globulin, but as an insoluble compound containing about 20 per cent. of nucleic acid. The following figures give the average of accordant analyses, calculated nucleic acid-free, of 18 different preparations representing complete as well as fractional precipitations under the above and other conditions. These figures agree closely with the composition of the leucosin of wheat, rye, barley, and malt.

LEUCOSIN.

Carbon	52.65
Hydrogen	7.04
Nitrogen	16.43
Sulphur	1.32
Oxygen	22.56
	<hr/>
	100.00

3. A *globulin*, precipitated in spheroids by dialysis and by dilution as a coherent deposit. The yield is about 5 per cent. of the embryo. The solution of this globulin in 10 per cent. sodium chloride brine becomes turbid on heating to about 87°, and at 90°, on continued heating, a considerable flocculent coagulum separates.

Our preparations of this globulin contained from 6 to 17 per cent. of nucleic acid, most of them from 12 to 15 per cent. From this the proteid could not be separated by fractional precipitation.

Analyses of ten different preparations of this globulin gave very closely agreeing figures when calculated free from nucleic acid, the average of which is as follows:

GLOBULIN.

Carbon	51.57
Hydrogen	7.07
Nitrogen	18.60
Sulphur	0.65
Oxygen	22.11
	<hr/>
	100.00

In composition and properties this globulin agrees with that found by the writer in the kernels of wheat, rye, and barley. So far as we have been able to observe, it differs from edestin, the crystalline globulin obtained from seeds of hemp, flax, and squash only in containing two-thirds as much sulphur.

4. *Proteose*, precipitated by saturating the aqueous extract, freed from globulin and albumin, with salt. One preparation, 35, was phosphorus-free, and had the following composition :

PROTEOSE.

Carbon	49.94
Hydrogen	6.80
Nitrogen	17.08
Sulphur	1.24
Oxygen	24.94
	<hr/>
	100.00

5. *Proteose*, soluble in the salt-saturated solution filtered from the foregoing proteose and obtained free from phosphorus by precipitating with alcohol its solution freed from salt by dialysis. The average of analyses of four preparations of this proteose is the following :

PROTEOSE.

Carbon	48.65
Hydrogen	6.75
Nitrogen	16.68
Sulphur	1.10
Oxygen	26.82
	<hr/>
	100.00

These proteoses together form about 3 per cent. of the embryo.

6. About one-third of the total nitrogen of the embryo is not extracted by water and salt solutions and appears to belong to insoluble compounds. This nitrogen is accompanied by phosphorus corresponding to about 6.75 per cent. of nucleic acid, which would contain two-thirds of this insoluble nitrogen. It seems probable, therefore, that this insoluble nitrogen belongs largely to insoluble compounds of nucleic acid and protein.

7. These phosphorus-containing preparations of globulin and leucosin, when digested with pepsin-hydrochloric acid, yield nuclein in proportion to the phosphorus which they contain. Calculated free from nucleic acid, the analyses of these nucleins show the protein constituent to have nearly the same composition as the proteid from which they were derived, the most marked difference being a greater proportion of sulphur in the former.

8. The proteids of the embryo differ from those of the dormant endosperm, of this as well as of other seeds, in the facility with which they undergo changes. These changes are the result of a redistribution of acids among the protein and other basic molecules, so that compounds form in the extracts of the embryo which contain various proportions of nucleic acid according to the changing conditions.

The writer has shown that the globulin, edestin, forms crystalline compounds with one and with two molecules of acid and also compounds with a greater number of acid molecules. There is reason to believe that all other native protein substances form similar compounds; in other words, that proteins are distinctly polyacid bases and that the acid characters which proteids display are due to acids united to their protein molecules probably in the same manner as in the salts of the purin bases.

These nucleic acid compounds of the protein constituents of the wheat embryo appear to be compounds of this order. According to this view, no special distinction can be made between nucleins and nucleoproteids, the former being simply compounds containing a greater number of molecules of nucleic acid united to one molecule of protein.

That the wheat embryo in fact contained the same nucleic acid *compounds* as we have obtained from the extracts, is highly

improbable. All that we can conclude is that the embryo contains the different protein substances described, together with nucleic acid, and that these may unite to form a number of different compounds according to the conditions which prevail at any given time.

THE PROTEIDS OF THE EGG YOLK.¹

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The yolks of a large number of freshly laid hens' eggs were broken up by straining through a sieve and mixed with an equal volume of saturated pure sodium chloride brine. A somewhat turbid solution resulted, which was shaken out with about one-third its volume of ether, containing a little alcohol. After standing one night, a clear reddish ethereal layer separated, leaving the pale yellow aqueous solution almost clear. After shaking out a second time with ether the aqueous solution was dialyzed for forty-eight hours, whereupon a large quantity of proteid separated in spheroids which united to a salvy mass. This was freed, as far as possible, from the liquid, by draining on filters, redissolved in 10 per cent. brine and its solution dialyzed for three days. From the semisolid mass thus obtained the liquid was decanted and the precipitate dissolved in 10 per cent brine. A little transparent gummy substance (lecithin?) remained undissolved which rendered filtration very difficult. By filtering under considerable pressure on a thick layer of paper pulp about 700 cc. of *perfectly clear* filtrate, *a*, and 2,000 cc. of very nearly clear filtrate, *b*, were obtained. The latter, *b*, was dialyzed for four days, when the large deposit was filtered out and treated with about a liter of salt solution. A gelatinous, almost pasty mixture resulted, which was shaken out with ether. The two liquids at once separated, the ethereal being clear and strongly yellow in color and the aqueous almost perfectly clear and not at all gummy. Shaken out three times more with ether, this aqueous solution became suddenly opaque and gelatinous. The mass was dialyzed free from chlorides, the solid deposit was washed with alcohol and with ether and dried over sulphuric

¹ From advance sheets of the report of the Connecticut Agricultural Experiment Station for 1899, communicated by the authors.

acid, giving preparation 1, weighing 60 grams. The *clear* solution, *a* (700 cc.), was diluted with three volumes of distilled water, and allowed to stand over night at a temperature of 6°. The proteid, which had separated on dilution, soon settled as a clear, transparent layer, from which the clear solution, *c*, was decanted completely. The proteid was readily and completely soluble in 10 per cent. brine to a perfectly clear pale yellow solution, which, when dialyzed until wholly free from chlorides, yielded the proteid in spheroids that subsequently united to a semisolid mass. The latter was filtered out, washed thoroughly with water and with alcohol, and dried over sulphuric acid, giving 32.1 grams of preparation 2. The solution, *c* (decanted from the precipitate produced by dilution that yielded 2), was treated with 1,000 cc. more water. This caused a precipitate which within two hours formed a semifluid deposit. From this the solution, *d*, was decanted, and the deposit dissolved in brine yielding a perfectly clear solution, which was dialyzed until free from chlorides.

The proteid thus precipitated was filtered out, washed with absolute alcohol as long as anything could be removed thereby, and then dried over sulphuric acid, giving preparation 3, weighing 16.5 grams.

The solution, *d*, was dialyzed free from chlorides, the precipitated spheroids were filtered out, washed with absolute alcohol and dried over sulphuric acid, making 5 grams of preparation 4.

The solution, page 413, filtered after forty-eight hours' dialysis from the substance that yielded the foregoing preparations, was further dialyzed until almost all its dissolved proteid had separated.

The precipitate thus produced was filtered out, dissolved in brine and the solution shaken out three times with ether. On shaking out the third time, the solution suddenly changed to an opaque jelly. This was then placed in a dialyzer, and when all the salt had been removed, the insoluble proteid was washed with absolute alcohol until everything soluble therein was extracted. Dried over sulphuric acid, this preparation, 5, weighed 75 grams. All these preparations were dried at 110° and analyzed with the following result:

	1	2	3	4	5
Carbon	50.82	51.21	51.10	50.69	50.48
Hydrogen	7.11	7.07	7.21	7.06	7.11
Nitrogen	16.04	16.11	16.23	16.40	15.50
Sulphur	1.11	1.05	1.00	1.05	1.02
Phosphorus	0.91	0.81	0.79	1.20	0.96
Ash	2.37	2.49	1.56	3.23	3.19
P ₂ O ₅ in ash	1.65	1.79	1.14	2.30	2.15

The ash of all these preparations consisted of sodium metaphosphate containing about 70 per cent. of P₂O₅. We have therefore subtracted from the total ash its phosphorus pentoxide, the remainder representing the ash to be deducted in calculating the percentage composition of the proteid substance.

Any chlorine or sulphur that might belong to the ash would necessarily be lost during incineration.

Calculating these preparations free from ash, as thus corrected, we have :

	1	2	3	4	5
Carbon	51.18	51.56	51.31	51.16	51.00
Hydrogen	7.14	7.12	7.24	7.12	7.18
Nitrogen	16.16	16.23	16.30	16.55	15.66
Sulphur	1.12	1.06	1.00	1.06	1.03
Phosphorus	0.92	0.82	0.79	1.21	0.97
Oxygen	23.48	23.21	23.36	22.90	24.16
	100.00	100.00	100.00	100.00	100.00

1 and 5 represent the two main fractions that weighed 60 and 75 grams respectively ; while 2, 3, and 4 represent fractions of 1, whose weights were respectively 32, 16.5, and 5 grams.

In composition all are nearly alike. A little more phosphorus was found in 4 than in the other preparations, probably because a larger proportion of some phosphorus-containing acid was combined with the protein of this final, very soluble fraction, which formed less than 10 per cent. of the total vitellin.

We have not yet succeeded in preparing this phosphorized acid free from proteid. The body, which we have thus prepared from egg yolk and analyzed, is not present, as such, in the egg, for the proteid substances of the yolk are readily and wholly soluble in salt solution, whereas all these preparations are entirely insoluble in salt solution. Insolubility in the cases of 2, 3, and 4 was caused by washing with alcohol, which at the

same time removed much lecithin. Lecithin was not present as an admixture, but was chemically combined with the proteid, forming a compound soluble in saline solutions and having the properties of globulin, as is shown by the following experiments.

A. The alcoholic washings from the three successive fractions, 2, 3, and 4, were evaporated and left residues of crude lecithin weighing 6.4796, 3.5913, and 1.3150 grams, respectively. Adding these quantities to the weights of the corresponding fractions dried at 110° , we have the amounts of lecithin-protein compound originally composing them. These contained 18.00, 19.4, and 22.23 per cent. of lecithin, respectively.

B. The yolks of two eggs were directly extracted with ether until practically nothing more was removed. The residual matter was then, as far as possible, dissolved in 10 per cent. salt solution, filtered perfectly clear and the solution diluted with water until an abundant precipitate separated. This was filtered out, dissolved in salt solution, and filtered perfectly clear. This solution and that filtered from the precipitate previously produced by diluting with water were separately dialyzed.

The proteid precipitates thus obtained were filtered out and washed with water and alcohol. The part precipitated by dilution was found to contain 17.5 per cent. of lecithin, that which remained in the diluted brine, 22.3 per cent.,—results in pretty close accord with those already stated.

C. Part of a large quantity of yolk vitellin which had suddenly become insoluble on shaking with ether, was thoroughly washed with water and then completely extracted with alcohol until all the lecithin, equal to 13.31 per cent. was removed. The solution, from which the above large quantity of insoluble proteid had originally separated, still contained a little protein matter and was therefore saturated with ammonium sulphate and the salt solution of the precipitate so produced was dialyzed. The substance which then separated in spheroids, after thorough washing with water, was still readily soluble in salt solution, but when washed with alcohol became insoluble and yielded to the alcohol 24.2 per cent. of lecithin.

Hoppe-Seyler considered this lecithin to be chemically combined with the proteid, with which view our experience is in full harmony. It is not possible that such large quantities of

lecithin are simply admixed with the protein matter, for were this the case it could be readily removed by ether. Furthermore we could not dissolve a mixture of globulin and lecithin in brine and obtain a clear solution easy to filter. That the proteid should unite with lecithin is to be expected, since protein readily combines with acids. We must, accordingly, consider the protein of egg yolk to be largely, if not wholly, a lecithin compound which dissolves in salt solution, and behaves like a globulin.

Saline extracts of egg yolk, like those of plant-seeds, contain, according to circumstances, mixtures of compounds of the protein molecule with several different numbers of molecules of lecithin, of which the more soluble compounds contain the larger number of acid molecules.

That we find such a large proportion of lecithin in these compounds is accounted for by its great molecular weight. If the molecular weight of the protein were 15,000,¹ its compound with four molecules of lecithin would contain over 17 per cent. of the latter.

Although we are not yet in a position to distinguish between these several compounds, it is nevertheless now necessary to make a distinction between the vitellin as it exists in the yolk, combined with lecithin, and the insoluble substance free from lecithin, which we have prepared and analyzed. As the designation vitellin has generally, if not always, been understood to apply to a protein substance, we suggest that this term be henceforth reserved for the protein, which in egg-yolk is united to lecithin and not to the compounds formed by their union, which may more properly be called lecithin-vitellin.

These considerations raise the question, are the preparations analyzed, vitellin, as defined above, or are they compounds of this protein with some other, at present unknown substance. Since the preparations yield paranuclein on digestion with pepsin, it appears highly probable that they contain paranucleic acid, but in less proportion than occurs in paranuclein.

To test this hypothesis we treated 10 grams preparation 5 with 100 cc. of N/10 potassium hydroxide solution, and after

¹ We have pointed out in a former paper (*This Journal*, 21, 486), the reasons which make it probable that the weight of the protein molecule may be about 15,000.

standing some time added enough 0.4 per cent. hydrochloric acid to neutralize the alkali and give an excess of acid equal to 0.2 per cent. of the solution. Pepsin was then intermixed and the solution digested at 40° for forty hours. After some time a voluminous precipitate separated from the nearly clear liquid. This was filtered out, washed thoroughly with water, and mixed with 45 cc. N/10 potassium hydroxide solution, which dissolved the precipitate and just neutralized its acid reaction to phenolphthalein. This solution was filtered perfectly clear and 45 cc. of N/10 hydrochloric acid were added, which threw out the paranuclein as a voluminous gelatinous precipitate. This was filtered out, washed thoroughly with water and with alcohol, and dried over sulphuric acid. This preparation, 6, weighed 2.38 grams. Another preparation of paranuclein was made by suspending 50 grams of preparation 5 in 0.2 per cent. hydrochloric acid, adding pepsin and, after digesting for twenty-four hours, adding more acid and pepsin and continuing the digestion twenty-four hours longer. The insoluble paranuclein was then filtered out, washed thoroughly with water and with alcohol, and dried over sulphuric acid. It weighed 15.7 grams. Preparation 7.

The yolks of 120 eggs were mixed with an equal volume of saturated sodium chloride brine and the mixture was shaken with ether containing a little alcohol. A perfectly clear red-yellow ether-layer and a clear pale yellow aqueous layer soon separated. The ether was drawn off and the aqueous solution again shaken with ether, which caused a part of the proteid to become insoluble, rendering the solution opaque and gelatinous. After the ether had separated, the aqueous solution was dialyzed until free from chlorides, when it was filtered and the very voluminous precipitate was suspended in 4 liters of 0.2 per cent. hydrochloric acid and digested with 3 grams of pepsin. After twenty-four hours the solution was decanted from a large deposit of insoluble matter; the latter was mixed with about one-third its volume of 0.4 per cent. hydrochloric acid and the digestion continued forty-eight hours longer, whereby the amount of insoluble matter was much reduced. The latter was then filtered out and repeatedly extracted with alcohol until the evaporated alcoholic washings left no residue. This required a

large quantity of alcohol and more than a week of time. The residue, air dried, weighed 32 grams and formed preparation 8.

These preparations were then dried at 110° and analyzed, with results as follows:

COMPOSITION OF PARANUCLEIN.

	6	7	8
Carbon	46.69	47.72	44.48
Hydrogen	6.77	6.80	6.52
Nitrogen	14.66	14.64	14.34
Sulphur	0.86	0.94	0.82
Phosphorus	3.29	2.52	4.19
Ash	1.89	5.01	3.43
P ₂ O ₅ in ash	0.83	2.47	1.61

Assuming that the yolk proteid and the paranuclein are both compounds of paranucleic acid, we should be able to calculate the composition of the protein substance in our preparations if we knew the composition of this acid. Unfortunately we do not know this acid in the free state.

Liebermann and others have thought that paranucleic acid is identical with metaphosphoric acid, but we think it extremely improbable that metaphosphoric acid can exist in animal tissues.

In seeking to harmonize the analyses of paranuclein with those of the paranucleoproteid we find that they are brought into more or less accordance by reckoning them free from ash and from certain phosphoric acid radicals. Assuming that the hydrogen of the phosphoric acid is replaced by protein, we have "corrected" our analyses for the following phosphoric acids; *viz.*, HPO₃, H₃PO₄, H₂P₂O₇, and H₄P₂O₇, by subtracting from the ash its P₂O₅ and to the remainder (the bases) adding the phosphorus and oxygen of the respective acids and, after deducting their sum from 100, recalculating these remainders to percentage statements.

Corrected for PO₃ we find no satisfactory agreement, as is shown by the following figures obtained by thus correcting the analyses of preparations 2 and 6.

	2	6
Carbon	52.68	50.86
Hydrogen	7.28	7.37
Nitrogen	16.57	15.97
Sulphur	1.08	0.94
Oxygen	22.39	24.86
	<hr/> 100.00	<hr/> 100.00

... these acids, however, we find a close agreement in the analyses of the preceding preparations in the following tables :

ANALYSES OF THE PARANUCLEOPROTEID AND THE PARANUCLEIN CALCULATED FREE FROM P_2O_5 AND ASH.

	Paranucleoproteid.			Paranuclein.		
	3	4	5	6	7	8
Carbon	52.99	53.14	52.57	52.54	53.17	52.12
Hydrogen	7.42	7.40	7.40	7.60	7.57	7.64
Nitrogen	16.70	17.19	16.11	16.50	16.31	16.80
Sulphur	1.03	1.10	1.06	0.96	1.05	0.96
Oxygen	22.26	21.17	22.86	22.40	21.90	22.48
	100.00	100.00	100.00	100.00	100.00	100.00

A comparison of these figures makes it plain that the paranuclein consists of one or more compounds of the protein (vitellin) containing a larger proportion of the same acid that exists in the paranucleoproteid from which it originated. These compounds with paranucleic acid are therefore analogous to the nucleic acid which we have obtained from the same source and described in the preceding paper.

Many seem to think, the paranucleic acid is not in fact identical with nucleic acid, but may be found to be either $\text{H}_2\text{P}_2\text{O}_7$ or $\text{H}_4\text{P}_2\text{O}_7$. These acids differ in composition so little from $\text{H}_3\text{P}_2\text{O}_7$, that we find nearly as close agreement when the analyses are calculated free from either of them, as the following table shows, in which is given the result of calculating the analyses free from P_2O_5 and ash.

ANALYSES OF THE PARANUCLEOPROTEID AND THE PARANUCLEIN CALCULATED FREE FROM P_2O_5 AND ASH.

	Paranucleoproteid.					Paranuclein.		
	1	2	3	4	5	6	7	8
Carbon	52.79	53.00	52.70	53.31	52.71	53.05	53.56	52.78
Hydrogen	7.39	7.32	7.44	7.42	7.42	7.69	7.63	7.74
Nitrogen	16.66	16.67	16.74	17.25	16.19	16.66	16.43	17.02
Sulphur	1.15	1.08	1.03	1.10	1.06	0.98	1.05	0.97
Oxygen	22.01	21.93	22.09	20.90	22.62	21.62	21.33	21.49
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Considering the great differences in phosphorus-content of these preparations, the striking agreement of the analyses thus

calculated makes probable that the acid combined with the protein has nearly the composition H_2PO_4 and contains little, if any, organic matter, or else contains an organic radical, whose composition is very nearly like that of the protein itself.

It may possibly be a methyl or ethyl phosphoric acid or some other quite simple organic phosphoric acid, but probably not so complex an acid as glycerophosphoric, as we have found a wide difference between the analyses when corrected for this acid.

It seems probable in view of these facts that further study will lead to the isolation and positive identification of this acid.

CONCLUSION.

Sodium chloride solutions dissolve from egg yolk a large amount of protein matter which has the properties of a globulin, being precipitated by diluting or dialyzing its solutions.

The substance soluble in salt solution consists of a mixture of compounds of protein matter with lecithin. Preparations of these compounds contain from 15 to 30 per cent. of lecithin. The more soluble products obtained by fractional precipitation contain larger proportions of lecithin than the less soluble; that is, they are more acid compounds. These compounds might well be called lecithin-nucleovitellin.

The lecithin thus combined is not removed by ether, but readily by alcohol. The insoluble lecithin-free proteid, obtained by treating the lecithin compounds with alcohol, has a constant composition when obtained from successive fractional precipitations of the lecithin compound. The following is the average of five accordant analyses representing fractional precipitations of the substance :

COMPOSITION OF NUCLEOVITELLIN.

Carbon	51.24
Hydrogen	7.16
Nitrogen	16.38
Sulphur	1.04
Phosphorus	0.94
Oxygen	23.24
	<hr/>
	100.00

This substance on digesting with pepsin yields paranuclein of variable composition. When the analyses of the nucleovitellin

and the paranuclein are calculated free from phosphoric acid, H_3PO_4 , possibly identical with "paranucleic acid", the composition found for the organic part of all of these preparations is so nearly the same as to show that the proteid and the nuclein are both compounds of one and the same proteid body, vitellin, with a phosphoric acid, possibly H_3PO_4 , $H_2P_2O_7$, or some very simple organo-phosphoric acid. The composition of the organic part of the preparations calculated free from H_3PO_4 gives as the average for eight preparations of the paranucleoproteid and the paranuclein, the following figures :

COMPOSITION OF VITELLIN.

Carbon	52.71
Hydrogen	7.46
Nitrogen	16.64
Sulphur	1.05
Oxygen	22.14
	<hr/>
	100.00

THE PROTEIN CONSTITUENTS OF EGG WHITE.¹

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

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A RECENT paper by the writer² gave an account of preparations of crystallized egg albumin which justified the conclusion that with the substance commonly called ovalbumin there is associated one or more other protein bodies, the properties of which were not definitely ascertained.

We have since repeated this work on a larger scale and have not only confirmed the former observations, but have obtained much additional information respecting these other protein bodies.

FRACTIONAL PRECIPITATION OF EGG WHITE.

Six liters of the whites of freshly laid eggs were gradually and carefully mixed with an equal volume of saturated ammonium sulphate solution and formed the precipitate, A, which was filtered off.

To the filtrate saturated ammonium sulphate solution was

¹ From advance sheets of the report of the Connecticut Agricultural Experiment Station for 1899, communicated by the authors.

² Report Conn. Agr. Exp. Station for 1898, and this Journal, 21, 486.

added until a small permanent precipitate was produced, and then a mixture of 600 cc. of saturated ammonium sulphate solution, 830 cc. of water, and 27 cc. of concentrated hydrochloric acid were gradually added. After standing over night, the large quantity of fine needle-shaped crystals which separated, fraction B, was filtered out.

The filtrate, mixed with saturated ammonium sulphate solution until a small precipitate again formed, was allowed to stand over night, during which time another crystalline precipitate, C, separated.

By treating the filtrate from C in the same manner, another precipitate, D, was obtained, which consisted wholly of spheroids.

All the protein matter which remained in the filtrate from D was precipitated by saturating the solution with ammonium sulphate, and this made preparation E. These several fractions were then further divided as follows:

Precipitate A was treated with water, strained with difficulty, owing to its gummy character, through bolting-cloth, and the slightly turbid solution thus obtained was dialyzed for several days. The considerable mucin-like precipitate which separated was filtered out, washed with much water, and dehydrated with absolute alcohol, giving 26.88 grams of preparation A.i.a.

The filtrate from the precipitate of A.i.a., saturated with ammonium sulphate, yielded a precipitate which was treated with a little water, and the part insoluble therein filtered out; the filtrate was allowed to evaporate until an amorphous precipitate separated. This precipitate was filtered out, united with the insoluble part of the ammonium sulphate precipitate, dissolved in water, and its solution dialyzed, yielding a precipitate which resembled that previously obtained by dialysis, being largely composed of gummy, mucin-like clots. This, when well washed with water and alcohol and dried, gave 7.28 grams of A.i.b. The dialyzed solution from which A.i.b. had separated, when treated with ammonium sulphate, yielded a precipitate which was filtered out, pressed on filter-paper, dissolved in water and this solution dialyzed free from sulphate. This dialyzed solution, evaporated at 40°, left a residue, marked A.2, weighing, dry, 16 grams.

The solution containing sulphate of ammonium, from which had been separated the substance yielding the two last-named preparations, was further concentrated by gradual evaporation, and yielded a mass of needle-shaped crystals. These were separated by filtration, dissolved in water, the solution was dialyzed till free from ammonium sulphate and evaporated at 40°, giving preparation A.3, weighing 11.56 grams.

Precipitate B.—This, consisting wholly of well-formed crystals, was dissolved in water and treated with saturated ammonium sulphate solution, which was added until precipitation began. After standing over night, the wholly crystalline precipitate was filtered out and the filtrate, marked b.2, treated as will be described later. The precipitate was again dissolved in water and enough ammonium sulphate added to give a precipitate from which, after a time, the solution was decanted. After pressing out the mother-liquor, the precipitate was dissolved in water and the clear solution dialyzed until wholly free from sulphate, when it was evaporated at 50°, giving 36 grams of B.1.

The filtrate from the precipitation of B.1 treated with more ammonium sulphate, on standing twelve hours, deposited a large crop of finely developed crystals. This was filtered out and, treated in the manner described for B.1, gave 59 grams of B.2. The filtrate from B.2 was added to solution b.2.

Precipitate C.—The filtrates from B.1 and B.2, forming solution b.2, were united with the aqueous solution of fraction C, ammonium sulphate was added to incipient precipitation and the mixture was allowed to stand over night. The substance, which separated in spheroids, was filtered out, dissolved in water and recrystallized by adding ammonium sulphate. On standing, the substance deposited in large aggregates of crystals, extending from the bottom of the dish in warty masses, some of them more than 2 cm. long and 0.5 cm. in diameter. These masses were wholly composed of exceptionally large and well-formed needle crystals. After separating from the mother-liquor, this crystalline mass was dissolved in water and the solution dialyzed till free from sulphate, and, evaporated at 50°, gave 45 grams of C.1.

The filtrate from C.1, on standing, yielded a very large quantity of substance which was composed almost wholly of crystals, only a very few spheroids being detected among them. This

precipitate, by the treatment applied to C.1, yielded 106 grams of C.2.

The filtrate from the first precipitation of C.1 was treated with more ammonium sulphate, the filtrate from C.2 was added, and the mixture allowed to evaporate slowly until a precipitate separated, which consisted of a mixture of crystals and spheroids. This yielded C.3, weighing 32.5 grams.

Precipitate D.—This was dissolved in water, ammonium sulphate solution was added and the mixture allowed to stand until a considerable separation of spheroids occurred, which, on settling, formed a clear, transparent deposit on the bottom of the dish.

After several reprecipitations, always without obtaining crystals, and thinking that the absence of crystals might be due to a deficiency of acid, we added to the solution 3 cc. of concentrated hydrochloric acid mixed with much ammonium sulphate solution. On standing, however, this solution, as before, deposited only spheroids. The deposit, after decanting the solution, was dissolved in water and its solution, after adding ammonium sulphate to incipient precipitation, was allowed to evaporate slowly. When considerable deposit had formed, the solution was decanted and allowed to concentrate until nearly all the remaining proteid matter had formed a coherent deposit of spheroids. These two deposits were each separately dissolved in water, their solutions dialyzed free from ammonium sulphate and evaporated to dryness at 50°, thus giving D.1, weighing 30 grams and D.2, weighing 20 grams.

The solution, decanted from the first precipitate which separated after adding acid, gave on evaporation a precipitate consisting wholly of spheroids, which formed D.3, weighing 55 grams. The solution from this, on further concentration, deposited nearly all the dissolved protein in the form of spheroids, which, by the usual treatment, gave 10 grams of D.4.

Precipitate E.—This, when dissolved in water, yielded a brilliant yellow solution, slightly acid to litmus. Thereto saturated ammonium sulphate solution, containing 1 cc. of concentrated hydrochloric acid, was added, which, on standing, caused a precipitate. This was filtered off, dissolved in water, ammonium sulphate was added to incipient precipitation, and after standing

seven days, the deposit of spheroids which had separated was filtered out, yielding 6.2 grams of E.1. The filtrate contained no protein matter.

The filtrate from the first reprecipitation of E was mixed with ammonium sulphate until a considerable amorphous precipitate had formed. This was filtered out, dissolved in water, and after adding ammonium sulphate and allowing the solution to stand six days, it gave a precipitate of spheroids which yielded E.2, weighing 15.65 grams.

The solution decanted from the first precipitation of E.2, after evaporating for six days, gave a deposit of spheroids mixed with a little amorphous matter, which was marked E.3, and weighed 22.5 grams.

We thus obtained from 6 liters of egg white, seventeen different fractions, containing 504 grams of substance, 262 grams of which were wholly crystalline, and since at least one-half of C.3 consisted of crystals, the total amount of crystalline matter was 278 grams. Evidently more than one-half the protein constituents of egg white can be crystallized. The yield of crystallized albumin was about the same as that obtained by the writer in his previous investigation, being about 4.4 grams of crystallized albumin per 100 cc. of egg white, as against 5.3 and 4.9 grams previously obtained.

Fractions E.2 and E.3.—Since the fractions E.2 and E.3 appeared, by their behavior on heating with water, to contain at least three protein substances, the greater part of each preparation was treated with water. E.2 contained some matter insoluble in water which could not be filtered out, while E.3 gave a clear solution. Both solutions, heated in a water-bath, gave a flocculent coagulum at 58° which, even after heating at 65° for some time, could not be filtered out. The temperature was therefore raised to 72° and held there some time, which caused more coagulum to separate in both solutions, but as the solutions could not even then be filtered, the bath was heated to boiling. With the rising temperature the coagulum rapidly increased, so that it could soon be filtered out on cloth. After thoroughly washing each coagulum with hot water and alcohol and drying over sulphuric acid, we obtained preparations E.2.a, weighing 6 grams, and E.3.a, weighing 8.6 grams. The clear, bright,

yellow filtrates from these were united and poured into several volumes of alcohol, which threw out a white precipitate and held the yellow coloring-matter in solution.

The precipitate, E.4, washed with alcohol and ether and dried over sulphuric acid, weighed 5 grams.

These preparations were then dried to constant weight at 110° and analyzed.

The heat coagulation points of their-solutions, containing 2.5 per cent. of the protein substance and 10 per cent. of sodium chloride, were determined by gradually heating in a water-bath. In Table I, page 428, T indicates the temperature at which the solution first became turbid, and F that at which flocks separated.

The specific rotation was determined with a Schmidt and Haensch polarimeter, the readings on the sugar scale being converted into degrees of circular polarization by multiplying by 0.346.

In the table the percentages of nitrogen marked K, were found by the Kjeldahl process, those marked A, by the Dumas or absolute method.

These results entirely confirm those given in our former paper, but in consequence of the more extended series of fractional-precipitations in the work now under discussion we have plainer evidence of the presence of the several protein constituents of the egg white.

Of these fractions, B.1, B.2, C.1, and C.2 consist of ovalbumin, separated in a completely crystalline condition, and, with the exception of a trace present in C.2, are wholly free from the lower coagulating albumin, thus demonstrating this latter to be a distinct substance. The rotation and elementary composition of these fractions are essentially the same as that given in our former paper for similar products.

In fraction E.4 we have ovomucoid not coagulated by heat, with a specific rotation of 61.5° and of the same composition as Möner¹ and Zanetti² found for this substance. The successive fractions, from C.3 to E.3.a inclusive, all have a higher specific rotation and contain a relatively considerable amount of an albumin coagulating at a much lower temperature than ovalbumin.

¹ *Ztschr. physiol. Chem.*, 18, 525.

² *Ann. di Chim. e Farmac.*, No. 12, 1897.

TABLE I.—THE WEIGHT, ROTATION, COMPOSITION, AND HEAT COAGULATION TEMPERATURES OF THE FRACTIONAL PRECIPITATES OF EGG WHITE.

Prepa- ration.	Weight Grams.	[α] _D .	Calculated ash-free.					Ash.	Coagula- tion tem- perature.	Remarks.
			C.	H.	N.	S.	P.			
A.1.a.	26.88	-21° 9'	50.69	6.71	14.49	2.280	trace	25.830	T 70° F 75°	Coagulum nearly disappears on boiling and reappears on cooling.
A.1.b.	7.28	...	50.95	6.85	14.82	1.938	none	25.442	1.41	...
A.2.	16.00	-31° 50'	52.76	7.12	15.48K 15.58K	1.687	0.123	22.770	0.41	T 64° F 70°
A.3.	11.56	...	52.40	7.12	15.77K 15.66K	1.729	0.002	23.029	0.28	T 66° F 70°
B.1.	36.00	-29° 53'	52.59	7.10	15.59K 15.51K	1.613	0.126	23.021	0.136	T 70° F 71°
B.2.	59.00	-29° 13'	52.78	7.09	15.54K 15.62A	1.619	0.127	22.814	0.150	T 68° F 70°
C.1.	45.00	-30° 2'	52.75	7.31	15.57A 15.43K	1.613	0.131	22.696	0.350	T 69° F 71°
C.2.	106.00	-30° 48'	52.79	7.00	15.57K 15.63A	1.634	0.126	22.850	0.20	T 62° F 65°
C.3.	32.40	-34° 2'	52.24	7.08	15.55A	1.755	0.085	23.290	0.290	T 57° F 57°
D.1.	30.00	-34° 18'	52.41	6.93	15.57A	1.796	0.106	23.188	0.14	T 51° F 55°
D.2.	20.00	-37° 14'	52.29	6.94	15.61A	1.886	0.062	23.212	0.04	...
D.3.	55.00	-41° 22'	51.62	6.94	15.23A 15.27K	1.972	0.048	24.170	0.10	T 52° F 55°
D.4.	10.00	-51° 30'	50.56	6.80	13.64A 13.54A	1.997 2.017	trace	27.033	0.11	T 62° F 64°
E.1.	6.20	-33° 30'	51.91	6.94	15.02A 15.27K	1.700 1.710	trace	24.285	0.49	T 59° F 60°
E.2.	15.65	-43° 7'
E.3.	22.50	-49° 5'
E.2.a.	6.00	...	52.40	6.91	15.69A	1.780	0.090	23.131	0.66	...
E.2.b.	8.60	...	51.94	6.84	15.31A	1.659	0.045	24.236	0.36	...
E.4.	5.00	-61° 30'	49.02	6.45	12.71A	2.379	0.11	29.441	0.750	...

No coagulum.

The fractions C.3, D.1, and D.2 have nearly the same rotation temperatures of coagulation and composition. We therefore subjected these to fractional precipitation, in order to determine whether they were mixtures of different proteids or were essentially one substance. The greater parts of these preparations were accordingly united, dissolved in about 400 cc. of water and saturated ammonium sulphate solution added, until a decided precipitate had formed. This was filtered out, freed from mother-liquor, dissolved in water, the solution dialyzed until free from ammonium sulphate and then evaporated to dryness below 50°. The residue, F.1, weighed 7.5 grams. The filtrate from F.1, on evaporating at the room temperature, deposited a quantity of spheroids, mixed with a few crystals of ovalbumin. This deposit was filtered out, dissolved in water, to the solution saturated ammonium sulphate solution was added until incipient precipitation set in, and the whole was allowed to stand until a considerable precipitate composed of spheroids mixed with a few crystals had formed. This was filtered out and, in order, if possible, to convert the whole into crystals, the original reaction of the egg white was imitated by making the aqueous solution of the precipitate slightly alkaline with ammonia. A very small excess of hydrochloric acid was added and then ammonium sulphate to incipient precipitation, thus reproducing, as closely as we could, the conditions under which the first crystalline separation had been obtained. After standing, a precipitate formed which contained no crystals. This was filtered out and, by the usual treatment, gave F.2, weighing 18.32 grams. The solutions filtered from the two preceding precipitations of F.2 were saturated with ammonium sulphate, and the resulting precipitate dissolved in water; its solution, dialyzed and evaporated below 50°, gave F.2.a, weighing 7.83 grams. The filtrate from the first precipitation of F.2 on further evaporation gave a precipitate of spheroids which was dissolved in water, and by the treatment employed for separating F.2.a, gave 16.7 grams of F.3.

The solution filtered from the second precipitation of F.3 was saturated with ammonium sulphate and from the precipitate produced by the usual treatment, F.3.a, weighing 5.38 grams, was obtained. These several preparations were found to have the

Correcting for the other three acids, however, we find a close agreement between all the analyses of the preceding preparations as is seen in the following tables :

COMPOSITION OF THE PARANUCLEOPROTEID AND THE PARANUCLEIN CALCULATED FREE FROM PO_4 AND ASH.

	Paranucleoproteid.					Paranuclein.		
	1	2	3	4	5	6	7	8
Carbon....	52.67	52.89	52.59	53.14	52.57	52.54	53.17	52.12
Hydrogen..	7.37	7.30	7.42	7.40	7.40	7.60	7.57	7.64
Nitrogen..	16.62	16.64	16.70	17.19	16.11	16.50	16.31	16.80
Sulphur...	1.15	1.09	1.03	1.10	1.06	0.96	1.05	0.96
Oxygen....	22.19	22.08	22.26	21.17	22.86	22.40	21.90	22.48
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The agreement of these figures makes it plain that the paranuclein consists of one or more compounds of the protein (vitellin) containing a larger proportion of the same acid that exists in the paranucleoproteid from which it originated. These protein compounds with paranucleic acid are therefore analogous to those with the nucleic acid which we have obtained from the wheat embryo and described in the preceding paper.

If, as many seem to think, the paranucleic acid is not in fact H_2PO_4 , it may be found to be either $\text{H}_3\text{P}_2\text{O}_7$ or $\text{H}_4\text{P}_2\text{O}_7$. These acids differ in composition so little from H_2PO_4 that we find nearly or quite as close agreement when the analyses are calculated free from either of them, as the following table shows, in which is given the result of calculating the analyses free from P_2O_5 and ash.

COMPOSITION OF THE PARANUCLEOPROTEID AND THE PARANUCLEIN CALCULATED FREE FROM P_2O_5 AND ASH.

	Paranucleoproteid.					Paranuclein.		
	1	2	3	4	5	6	7	8
Carbon	52.79	53.00	52.70	53.31	52.71	53.05	53.56	52.78
Hydrogen....	7.39	7.32	7.44	7.42	7.42	7.69	7.63	7.74
Nitrogen.....	16.66	16.67	16.74	17.25	16.19	16.66	16.43	17.02
Sulphur	1.15	1.08	1.03	1.10	1.06	0.98	1.05	0.97
Oxygen.....	22.01	21.93	22.09	20.90	22.62	21.62	21.33	21.49
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Considering the great differences in phosphorus-content of these preparations, the striking agreement of the analyses thus

calculated makes probable that the acid combined with the protein has nearly the composition H_2PO_4 and contains little, if any, organic matter, or else contains an organic radical, whose composition is very nearly like that of the protein itself.

It may possibly be a methyl or ethyl phosphoric acid or some other quite simple organic phosphoric acid, but probably not so complex an acid as glycerophosphoric, as we have found a wide difference between the analyses when corrected for this acid.

It seems probable in view of these facts that further study will lead to the isolation and positive identification of this acid.

CONCLUSION.

Sodium chloride solutions dissolve from egg yolk a large amount of protein matter which has the properties of a globulin, being precipitated by diluting or dialyzing its solutions.

The substance soluble in salt solution consists of a mixture of compounds of protein matter with lecithin. Preparations of these compounds contain from 15 to 30 per cent. of lecithin. The more soluble products obtained by fractional precipitation contain larger proportions of lecithin than the less soluble; that is, they are more acid compounds. These compounds might well be called lecithin-nucleovitellin.

The lecithin thus combined is not removed by ether, but readily by alcohol. The insoluble lecithin-free proteid, obtained by treating the lecithin compounds with alcohol, has a constant composition when obtained from successive fractional precipitations of the lecithin compound. The following is the average of five accordant analyses representing fractional precipitations of the substance :

COMPOSITION OF NUCLEOVITELLIN.

Carbon	51.24
Hydrogen	7.16
Nitrogen	16.38
Sulphur	1.04
Phosphorus	0.94
Oxygen	23.24
	<hr/>
	100.00

This substance on digesting with pepsin yields paranuclein of variable composition. When the analyses of the nucleovitellin

filtered clear and heated to 60° . The coagulum was washed with salt solution, suspended in water after passing through fine bolting-cloth to break up all lumps, washed thoroughly with water, and with alcohol, and was dried, giving 2.78 grams of K.3.1. Unlike ovalbumin, this coagulated proteid separated in a finely divided state, so that it could be easily washed through the cloth.

The filtrate from this coagulum was dialyzed free from chlorides and then evaporated to dryness below 60° , leaving a residue which weighed 17.2 grams and had a specific rotation of $37^{\circ} 55'$. This rotation being much greater than that of ovalbumin, the whole of this residue was dissolved in 10 per cent. brine, the solution heated in a boiling water-bath, the coagulum, K.3.2, filtered off, the filtrate dialyzed free from chloride, and the clear solution poured into alcohol. The substance, K.3.3, thus precipitated, weighed, dry, 1.39 grams, and consisted of ovomucoid as shown by its rotation, $61^{\circ} 30'$.

The preparation, K.3, was prepared from the precipitate produced by half saturating the egg white solution with ammonium sulphate, which precipitate is commonly supposed to consist almost wholly of globulin. Nevertheless our results show that K.3 contained about 11 per cent. of the albumin coagulating below 65° , 83 per cent. of ovalbumin, and over 5 per cent. of ovomucoid. That so much of this latter substance should be present in this preparation is surprising and shows the difficulty in separating ovomucoid from ovalbumin.

All these preparations were analyzed with the results given in Table III.

These figures show that an albumin coagulating at 55° – 57° forms nearly 50 per cent. of the products obtained from D.3. This albumin contains somewhat less carbon, decidedly more nitrogen, and a little more sulphur than ovalbumin. Since it so closely resembles ovalbumin, and is so intimately associated with it the writer suggests that it be called *conalbumin*. The rest of the products from D.3 consists of about 35 per cent. ovalbumin and 18 per cent. ovomucoid. From F.3, 27 per cent. of conalbumin, 31 per cent. of ovalbumin, and 20 per cent. of ovomucoid were obtained.

This investigation of the protein constituents of the egg white

TABLE III.—COMPOSITION, ETC., OF PRODUCTS DERIVED FROM FRACTIONS D, F, AND K.

Preparation.	Weight, grams.	[η] _D .	Ash free.					Ash.	Coagulation temperature.	Remarks.
			C.	H.	N.	S.	P.	O.		
D.3.1.	5.00	52.19	6.84	16.10K	1.67	0.010	23.19	0.85	{ T 48° F 52° Formed about 48 per cent. of D.3.
D.3.2.	3.81	52.08	7.04	15.36	1.61	0.110	23.80	0.23	{ T 64° F 70° Formed about 35 per cent. of D.3.
D.3.3.	2.00	61°10'	48.90	6.61	12.16K	2.34	none	29.99	2.33	{ No coagulum. Formed about 18 per cent. of D.3.
F.3.1.	1.87	{ 16.03K 16.15K	17.3	trace	1.19	{ T 58° F 59° Formed about 27 per cent. of F.3.
F.3.2.	2.17	15.16K	1.61	2.00	{ T 70° F 70° Formed about 31 per cent. of F.3.
F.3.3.	1.39	61°20'	{ No coagulum. Formed about 20 per cent. of F.3.
K.3.1.	2.78	52.31	7.05	16.16K	1.71	trace	22.77	0.56	{ T 57° F 60° Formed about 11 per cent. of K.3.
K.3.3.	1.39	61°30'	{ Formed about 5.5 per cent. of K.3.

shows them to be ovomucin, ovalbumin, conalbumin, and ovomucoid. These have the following properties :

Ovomucin is a glycoproteid recently discovered by Eichholz¹ to be present in small amount in egg white. This substance, precipitated by diluting egg white, has heretofore been regarded as globulin, but we find that nearly, if not quite, all of that which is so precipitated, is ovomucin.

From the whites of 240 eggs we obtained, although with some loss, 34.2 grams of ovomucin or about 7 per cent. of the proteid matter of the egg white, which is the proportion in which Dillner found the "globulin" to be present.

When freshly precipitated by dilution or dialysis, ovomucin loses its gummy character on thoroughly washing with water, but, when treated with salt solutions, forms a transparent gummy mass, which, on agitation, yields a clear but viscid solution.

When washed with alcohol and dried, ovomucin forms a light, white powder, partly soluble in sodium chloride brine, and gives a solution free from viscosity, which becomes turbid at 75°, and yields flocks at 78°. On boiling, this coagulum almost wholly dissolves and reappears on cooling.

Eichholz states that ovomucin dissolves in dilute sodium carbonate solutions. We find, however, that when treated with much 1 per cent. sodium carbonate, only an apparent solution results, for, when this is brought into filters, a clear, thin liquid passes through the paper from which, by adding acid, only an insignificant precipitate can be obtained, while a clear and very viscid liquid, containing almost all the ovomucin, remains upon the paper.

We have made, page 423, two preparations of ovomucin which had the following composition :

OVOMUCIN.		
	A. I. a.	A. I. b.
Carbon	50.69	50.95
Hydrogen	6.71	6.85
Nitrogen	14.49	14.82
Sulphur	2.28	1.94
Oxygen.....	25.83	25.44
	<hr/> 100.00	<hr/> 100.00

¹ *Jour. of Physiology*, 23, 167.

Ovalbumin is the chief constituent of egg white, 50 per cent. of its proteids having been obtained in this investigation in the form of perfectly crystallized preparations of this substance, while a large proportion of the remaining proteid matter also consisted of this albumin.

Heat Coagulum of Ovalbumin.—Solutions in pure water, containing 2.5 per cent. of pure ovalbumin, become turbid at 60°, and at 64° yield a flocculent coagulum.

When 10 per cent. of sodium chloride is added to these solutions the temperature of coagulation becomes higher, turbidity developing at 69°, and flocks at 70°.¹

When its solution is evaporated to dryness below 50°, and the ovalbumin redissolved in water or in brine, a small amount of substance coagulating at the lower temperature appears to be formed. Thus, sodium chloride solutions containing 2.5 per cent. of B.1, B.2, or C.1, before these substances had been separated by evaporation at 50°, remained absolutely clear until heated to 68° or 69°, while similar solutions, made by dissolving the dried substance, became turbid at 59° and yielded flocks in small quantity at 63°.

Preparations of ovalbumin obtained by evaporating their solutions in pure water to dryness below 50°, do not completely redissolve when treated with water.

Solutions of some preparations thus made, become very rapidly turbid when filtered and gradually deposit a not inconsiderable quantity of insoluble matter. The amount of insoluble matter in all of our preparations was so small, that we have been unable to learn its nature, but in one case we obtained 0.72 gram from 15 grams of a preparation containing a larger proportion than any we had seen before. This insoluble substance, which contained 15.65 per cent. nitrogen, and 1.8 per cent. sulphur, was probably a mechanical coagulum, as it tended to separate at points of contact between the surface of the albumin solution and the vessel containing it. Sodium chloride added to the solution in sufficient quantity diminishes the amount, or prevents its formation.²

¹ Stärke (Pflüger's *Archiv.*, 12, 18) notes this effect of sodium chloride on the coagulation of the albumin.

² See Hopkins : *Jour. of Physiology*, 25, 324.

It has been stated by Hammarsten that with a constant amount of salt the temperature of coagulation changes with variable amounts of albumin in solution.

We, accordingly, prepared solutions of the dialyzed, but not dried, albumin which contained 5, 2.5, and 1.0 per cent. of ovalbumin and also similar solutions containing, in addition, 10 per cent. of sodium chloride. These, when heated very slowly in a large water-bath, coagulated as follows:

		Water.	10 per cent. salt solution.
5.0 per cent. albumin	turbidity.....	59°	68°
	flocks.....	64°	71°
2.5 " " "	turbidity.....	60°	69°
	flocks.....	64°	71°
1.0 " " "	turbidity.....	61°	69°
	flocks.....	67°	71°
0.5 " " "	turbidity.....	63°	..
	flocks.....	none even on boiling.	

These figures show no difference in temperature of coagulation, for solutions containing from 1 to 5 per cent. of ovalbumin, together with 10 per cent. of sodium chloride, but solutions of ovalbumin in pure water coagulate at a lower temperature than those containing 10 per cent. of this salt; those containing 5 and 2.5 per cent. of albumin, coagulate at one and the same temperature; those containing 1 per cent. coagulate somewhat higher, while a solution containing but 0.5 per cent. of albumin yields no flocks even on boiling.

When the proportion of albumin remains constant, while that of the salt increases, the temperature of coagulation rises, as the following table shows:

NaCl. Per cent.	Ovalbumin. Per cent.	
1.0	2.5	{ 61° turbidity. 63° flocks.
3.0	2.5	{ 63° turbidity. 65° flocks.
5.0	2.5	{ 65° turbidity. 67° flocks.
10.0	2.5	{ 68° turbidity. 70° flocks.

From these results we may state that solutions in water which contain from 2.5 to 5 per cent. of pure ovalbumin become turbid on heating to 60°, and yield a flocculent coagulum at 64°.

while those containing, in addition, 10 per cent. of sodium chloride become turbid at 68°, and flocculent at 70°.

In the preceding experiments no acid was added to the solution to be coagulated, the acidity of the ovalbumin (1 gram of albumin required 2 cc. of N/10 alkali for neutralization to phenolphthalein) being sufficient to bring about coagulation.

When the albumin was exactly neutralized to phenolphthalein, by adding potash, the solution remained clear when heated for some time at 100°. When this solution was treated with acid equivalent to the added alkali a large precipitate resulted which did not separate completely until a very slight excess of acid was added. Thus, when 0.5 gram of albumin was dissolved in 19 cc. of water, 1 cc. N/10 potassium hydroxide added, making the solution exactly neutral to phenolphthalein, and the mixture heated for ten minutes in boiling water, no coagulum was produced. When cooled, 1 cc. of N/10 hydrochloric acid was added, which gave a precipitate, from which a clear filtrate could not be obtained; with 1.2 cc., however, the precipitation was so complete that the filtrate gave no turbidity with alcohol. When 1 gram of albumin was dissolved in water and 2 cc. of N/10 ammonia solution were added, a quantity just sufficient to neutralize the acid reaction of the albumin, the solution remained clear after heating for some time at 100°. After cooling, on adding N/10 hydrochloric acid, the solution remained clear until nearly enough acid had been added to neutralize the 2 cc. of ammonia, but when the full 2 cc. were added the albumin was so completely precipitated that the solution filtered from the coagulum contained only a trace of protein matter. The solution, thus neutralized with either potash or ammonia, gave off hydrogen sulphide when heated and acidified.

To six tubes, each containing 0.5 gram of albumin, dissolved in 10 cc. of water, were added respectively 0.2, 0.4, 0.6, 0.8, 1, and 1.1 cc. N/10 hydrochloric acid, and then water enough to make each up to 20 cc. When these mixtures were heated in boiling water, the one with 0.8 cc. of acid yielded some coagulum, that with 1 cc. but a trace, while that with 1.1 cc. remained clear, showing 1 cc. of N/10 hydrochloric acid to be enough to convert 0.5 gram of albumin into a compound not coagulated by heat. The portions with 0.2 and 0.6 cc. were com-

pletely, while that with 0.8 cc. was incompletely, coagulated. When 0.5 gram of albumin was dissolved in 20 cc. of water, containing from 0.5 cc. to 3 cc. of N/10 acetic acid and heated in a boiling water-bath, the albumin was practically completely coagulated; with 5 cc. of acetic acid the solution became opalescent at 64°, and formed a firm, transparent jelly at 75°. On heating at 99° with 10 cc. of N/10 acetic acid the solution formed a clear, thin jelly.

When solutions in pure water of any of our purest preparations of ovalbumin were heated to boiling for some time the albumin was so incompletely coagulated that a clear filtrate could not be obtained.

Six 2-gram portions of pure ovalbumin, were dissolved, each in 100 cc. of water, and mixed with equal volumes of water, containing 1, 2, 3, 4, 5, and 6 cc. of N/10 acetic acid respectively, and the mixtures boiled and poured on filters. The portion with 1 cc. of acid clogged the filter, as the coagulum separated imperfectly, whereas the others yielded clear filtrates. These, when evaporated to dryness, left residues weighing 0.0492, 0.0332, 0.0320, 0.0446, and 0.0648 gram, respectively.

From this it is seen that with 1 cc. of N/10 acetic acid the coagulation is incomplete, while with 3 and 4 cc. the amount of matter remaining in solution is less than with 2 cc. or than with 5 and 6 cc. This dissolved matter, which is very soluble in water, yields a solution decidedly acid to phenolphthalein and to litmus, contains proteid, and reduces Fehling's solution. Since the proportion, in which it is produced, appears to depend upon the quantity of acid added, we are inclined to regard it chiefly as a product of the action of the added acid upon a small part of the albumin, whereby uncoagulable acid compounds are formed in small, but variable proportion.

Specific Rotation.—This was determined for solutions of the ovalbumin in pure water, with a Schmidt and Haensch polarimeter, the readings of the sugar scale being converted into degrees of circular polarization by multiplying by 0.346, and the amount of dissolved albumin ascertained by evaporating and drying the residue at 110°. Preparations B.1, B.2, C.1, and C.2 showed very nearly the same rotation as that found by us in our

former work for preparations of pure ovalbumin. These determinations gave the following values for $[\alpha]_D$.

A.1 ¹	-29.31°	B.1.....	-29.53°
A.2 ¹	-29.40°	B.2.....	-29.13°
H.1 ¹	-28.60°	C.1.....	-30.03°
H.2 ¹	-29.81°	C.2.....	-30.80°

The degree of rotation was found to be the same in sodium chloride solutions as in water, and also to be the same for the albumin in the dialyzed solutions of the crystals, as in solutions of the albumin which had been separated from such solutions by evaporation at 50°.

Since this paper was written we have received the number of the *Journal of Physiology* issued April 24, 1900, containing a paper on "Pure Albumin", by F. G. Hopkins, in which he gives the rotary power of pure albumin as -30.70° . The remarkable agreement between the rotation of the many fractional crystallizations, obtained by Hopkins, is much closer than between those observed by us, which is probably due to his superior polariscope and to the stronger solutions of the albumin, containing considerable amounts of ammonium sulphate, which he employed. Because solutions rich in pure albumin, when free from salts, are not easily obtained absolutely clear and tend to become turbid, probably from mechanical coagulation, we were generally not able to use solutions so rich in albumin as those employed by Hopkins. The difference of 1.3° between the values of $[\alpha]_D$ found by Hopkins and the writer, is probably chiefly due to the different methods employed for determining albumin in the solution examined. We have shown, page 438, that when ovalbumin is coagulated in the presence of a minimum of acetic acid, about 1.5 per cent. of uncoagulated matter remains in solution. Whether this occurs under the conditions under which Hopkins coagulated his albumin requires further investigation. Hopkins admits that the method employed by us is the more accurate, assuming that all ammonium sulphate can be separated from the albumin solution. We believe that we have accomplished this in view of the great care we have taken to detect the presence of sulphates in our albumin preparations and feel quite sure that we have not overlooked a quantity of ammo-

¹ These are preparations of the old series formerly described, and the two first are not parts of fraction A of the present series.

nium sulphate sufficient to have caused a difference of 4 per cent. of the observed rotation.

Elementary Composition.—In the following table we give the analyses of our four purest preparations of ovalbumin, and also analyses of two preparations made by Hofmeister's method as described on page 441.

COMPOSITION OF OVALBUMIN.

	B.1.	B.2	C.1.	C.2	No. 2.	No. 3.	Average.
Carbon.....	52.59	52.78	52.75	52.79	52.82	52.78	52.75
Hydrogen...	7.10	7.09	7.31	7.00	7.03	7.07	7.10
Nitrogen....	15.55	15.57	15.50	15.60	15.32	15.53	15.51
Sulphur.....	1.613	1.619	1.613	1.634	1.590	1.651	1.620
Phosphorus .	0.126	0.127	0.131	0.126	0.123	0.112	0.122
Oxygen	23.021	22.814	22.696	22.850	23.117	22.857	22.898
	100.000	100.000	100.000	100.000	100.000	100.000	100.000

ANALYTICAL METHODS.

Carbon and hydrogen were determined by using an open tube with copper oxide, lead chromate, and metallic copper, and finishing the combustion in oxygen.

Nitrogen was determined by Dumas' method, the air being removed by a Sprengel pump, the tube then filled with carbon dioxide set free by heating sodium bicarbonate at the front end, again emptied by the pump and this process repeated. In this way all the air was removed and no fixed gas was driven off on heating the reagents. Nitrogen was also determined by the Kjeldahl method and results in close accord with those of Dumas' method were obtained.

Sulphur was determined by fusing about 1 gram of the substance with sodium hydroxide and peroxide over an alcohol lamp. The reagents were proved to be free from sulphur.

Phosphorus was determined by fusing about 1 gram of the substance with sodium peroxide, dissolving the fusion in nitric acid, precipitating with molybdic solution and weighing as magnesium pyrophosphate.

The figures given in the above table agree well with those of others who have prepared and analyzed ovalbumin with especial care as may be seen in the following table :

COMPOSITION OF OVALBUMIN.

	C.	H.	N.	S.	P.	O.	
Hammarsten	52.25	6.90	15.25	1.64	...	23.69	uncoag.
Chittenden and Bolton....	52.33	6.98	15.89	1.83	...	22.97	"
" "	52.33	6.98	15.84	1.81	...	23.04	coag.
Bondzinski and Zoja.....	52.39	7.11	15.39	1.66	...	23.45	"
Osborne and Campbell....	52.75	7.10	15.51	1.62	0.12	22.90	
Hopkins.....	52.75	7.12	15.43	1.57			

There would be no longer any question about the composition of ovalbumin, were it not for Hofmeister's¹ analysis of a single preparation, and the recent assertion of Schulz,² that on crystallizing by the "acid process" a hydrate of Hofmeister's egg albumin is formed. This we have shown in our former paper to be untrue, for we there gave the results obtained by analyzing a preparation made exactly according to Hofmeister's method, which agreed quite well with the analyses of all our other preparations made by the acid method of Hopkins.

That there should be no question as to the composition of crystallized ovalbumin made according to Hofmeister's method we made preparation No. 2, recrystallized six times and coagulated by alcohol, No. 3, by recrystallizing four times, pressing the crystals on filter-paper, dissolving them in water, dialyzing the solution perfectly free from sulphate and evaporating the filtered solution at 50° to dryness.

Dried at 110° these preparations were found to have the following composition:

COMPOSITION OF OVALBUMIN CRYSTALLIZED BY HOFMEISTER'S METHOD.

	No. 2.	No. 3.	Average of the analyses given on page 365.
Carbon	52.82	52.78	52.75
Hydrogen	7.03	7.07	7.10
Nitrogen	15.32	15.53	15.51
Sulphur	1.590	1.651	1.62
Phosphorus	0.123	0.112	0.12
Oxygen	23.117	22.857	22.90
	100.000	100.000	100.000

These analyses are in almost exact agreement with the average given in the preceding table, and fail to confirm Hofmeister's figures for sulphur, or the conclusions drawn by him and by Schulz respecting the relation of the crystallized albumin to that heretofore obtained by other methods. The percentage of carbon found by us falls midway between that given by Hofmeister and the average of that given by the other investigators, with the exception of Hopkins. The very close agreement in composition between all the many fractions, having a constant rotatory power, analyzed by Hopkins and by ourselves, leaves

¹ *Ztschr. physiol. Chem.*, 16, 187.

² *Ibid.*, 29, 86.

little doubt as to the true elementary composition of crystallized ovalbumin, especially in view of the close agreement of these analyses with those of Hammarsten and of Bondzynski and Zoja.

In view of the statements recently made by Schulz concerning the proportion of sulphur in ovalbumin,¹ we used the very greatest care in determining this element. Our solutions of albumin were not only dialyzed until they gave no reaction with barium chloride, but until no sulphate could be detected in the water outside of the dialyzer, even after concentration. That our higher figures for sulphur are not due to ammonium sulphate, which could not be separated from the albumin by dialysis, is disproved, not only by the close agreement between our many analyses, but also by the fact that we obtained exactly the same figures from preparations free from conalbumin and ovomucoid, made by coagulating their dilute solutions at 70°-95°. Thus, we found in D.3.2, 1.61, in F.2.1, 1.64, in F.3.2, 1.61, and in E.3.2, 1.63 per cent. We have no doubt that these figures very closely represent the true proportion of sulphur contained in the ovalbumin, especially as they agree with the figures which Hammarsten obtained,² by four different methods; namely, 1.67, 1.67, 1.62, and 1.58 and also with those of Bondzynski and Zoja. The results obtained by Hopkins,³ which have come to our notice since this paper was written, leave no doubt whatever that the true proportion of sulphur is very close to 1.60 per cent., Hopkins finding an average of 1.57 per cent. while we find 1.62 per cent., the slight difference between our results being doubtless due to slight differences in our methods of operation.

It is to be noted that we have found a small but uniform quantity of *phosphorus* in all our preparations of crystallized albumin. In Table I, page 428, it is seen that the four crystallized preparations, B.1, B.2, C.1, and C.2, all contained 0.12 per cent. of phosphorus, whereas all the other non-crystalline preparations contained less, the amount diminishing as the proportion of ovalbumin diminished in the successive fractions. In Table

¹ *Ztschr. physiol Chem.*, 28, 16; 29, 86.

² *Ibid.*, 9, 304.

³ *Jour. of Physiology*, 28, 306.

III, page 432, it appears that D.3.1, consisting of conalbumin, contained but 0.01 per cent., whereas D.3.2, consisting of coagulated ovalbumin, contained 0.11 per cent., and D.3.3, consisting of ovomucoid, contained but a trace.

In our earlier series of preparations, this phosphorus was found in the ash, as calcium phosphate; in our present series, only a part of it was present in the ash, in which it occurred as sodium or potassium metaphosphate.

As our former series of preparations were dialyzed in river water containing calcium bicarbonate and our later series in distilled water, it seems highly probable that this phosphorus belongs to an acid united with the crystallized albumin in the same manner as the writer has shown that hydrochloric acid unites with edestin to form crystalline compounds.¹

As to the nature of this phosphorized acid we have learned nothing, owing to the small proportion in which it is present.

THE CARBOHYDRATE SPLIT FROM THE OVALBUMIN BY BOILING WITH ACIDS.

These purest preparations of ovalbumin, which we have shown to have a constant specific rotation, the same composition and the same temperature of coagulation, when boiled with acids, all give solutions which yield considerable quantities of crystalline precipitates with phenylhydrazine.

When boiled with 3 per cent. hydrochloric acid for thirty minutes, the solution obtained reduces Fehling's solution, but fails to do so after boiling for three hours. The addition of Fehling's reagent to such solutions causes an intense biuret reaction, but no reduction of the copper salt takes place, even after adding considerable quantities of glucose. Evidently, by continued boiling, some substance is produced which prevents the reduction of the Fehling's solution. Blumenthal and Mayer² state that after long boiling this reduction is not so easily detected as after boiling for a short time.

Ten grams of each of the four preparations, B.1, B.2, C1, and C.2, were boiled with 200 cc. of 9 per cent. sulphuric acid for three hours and the solutions neutralized to litmus with baryta. The soluble matter was filtered out, washed with water, and the filtrate

¹ This Journal, 21, 486.

² *Ber. d. chem. Ges.*, 32, 274.

and washings were evaporated to a volume of 100 cc. To this solution 10 grams of sodium acetate were added and 5 cc. of a mixture of equal volumes of phenylhydrazine and 99 per cent. acetic acid, and the whole heated for three hours in boiling water. After standing over night, the crystalline precipitates were filtered off and washed rapidly with water and then with absolute alcohol, which removed a considerable quantity of deep red-colored, amorphous substance. The washed precipitates were then dried at 110° and weighed.

In order to learn the effect of the presence of ovomucoid, upon this precipitation with phenylhydrazine, 10 grams of G.4, which had a specific rotation of $39^{\circ} 22'$, and contained much ovomucoid, were treated in the same manner as these albumin preparations and at the same time with them.

For comparison, 100 cc. of a solution containing 1 gram of glucose were treated with phenylhydrazine under the same conditions. The filtrate from each phenylhydrazine precipitate was further treated with 5 cc. of phenylhydrazine and 10 grams of sodium acetate and a second precipitate obtained. From the filtrates from the second precipitations no more could be separated by further additions of phenylhydrazine. The weight of each precipitate dried at 110° , is given in the following table:

	B.1.	B.2.	C.1.	C.2.	G.4.	Glucose.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
1st	0.2019	0.1327	0.1831	0.0902	0.2175	0.3098
2nd ...	0.1030	0.1027	0.0980	0.0281	0.2684	0.3187
	<u>0.3049</u>	<u>0.2354</u>	<u>0.2711</u>	<u>0.1183</u>	<u>0.4859</u>	<u>0.6285</u>

Since from C.2 we got so much less of this substance than from the others, we repeated this experiment, using for the first precipitation 10 cc. of the phenylhydrazine-acetic acid mixture and 20 grams of sodium acetate. In this way we got

	C.2.	Gram.
1st		0.1787
2nd		0.0894
		<u>0.3681</u>

The crystals of the osazone obtained from the albumin consisted of feathery sprays and always appeared distinctly differ-

ent from the aggregates of needles yielded by glucose. Two different preparations of the phenylhydrazine compound were separately recrystallized by dissolving in boiling absolute alcohol, adding water, boiling until most of the alcohol had been expelled, and then allowing the solution to cool slowly until the substance separated in beautiful, yellow crystals of the same form as the original precipitate. These melted at 187° and 189° .

The amount of this osazone indicates that a considerable quantity of carbohydrate is split from our albumin preparations by boiling with acids. The quantity of osazone which we obtained from our preparations varied from one-third to one-half of that given by 1 gram of glucose under like conditions, and if the compound from the albumin is precipitated in the same proportion as the glucosazone we may infer that the albumin yields on hydrolysis from 3 to 5 per cent. of carbohydrate. The amount of osazone which we have actually obtained corresponds to from 2-2.5 per cent. of carbohydrate calculated as glucose. Hofmeister¹ obtained from 1 gram of ovalbumin 0.13 gram of osazone, from which he infers the presence of 15 per cent. of carbohydrate.

Does this carbohydrate come from the ovalbumin or from a residue of ovomucoid which we have not separated by our fractional crystallizations? Seemann² obtained a copper oxide reduction from ovomucoid corresponding to 34.9 per cent. of glucose. If this proportion is correct, we must have at least 6 per cent. of ovomucoid in our albumin preparations, to account for the minimum yield of osazone, corresponding to 2 per cent. of carbohydrate. This is probably the least quantity of ovomucoid which could yield this quantity of osazone. From the incompleteness of precipitation of osazone, it is probable that the quantity of ovomucoid would have to be more than twice as great to yield the quantity of osazone found. From G.4, which had a specific rotation of $39^{\circ} 22'$, we obtained nearly twice as much osazone as from the ovalbumin, due unquestionably to the presence of ovomucoid in this preparation. If this increased yield of osazone is attended by an increase of 10° in the rotation, an admixture of ovomucoid sufficient to yield such quantities of

¹ *Ztschr. physiol. Chem.*, 24, 170.

² *Archiv. f. Verdauungskrankheit*, 4, 275.

osazone would manifest itself by variations in the rotation of these albumin preparations, it being improbable that so much ovomucoid was admixed in uniform proportion in the successive crystallized precipitates. We have shown on page 438 that the preparations of ovalbumin when coagulated by heat, left in solution a small quantity of uncoagulable matter amounting to about 1.6 per cent. of the albumin, the nature of which we have been unable to discover, owing to its small quantity. It may be ovomucoid, since it contains proteid matter and yields a copper-reducing body on boiling with acids, but in general appearance and manner of dissolving it does not behave like ovomucoid. As already stated on page 439, we think it more probable that this substance is a product of the action of acetic acid, whereby a small quantity of uncoagulable acid compounds of the albumin is formed. Hydrochloric acid, added in the same proportion as acetic acid, converts, in the absence of soluble salts, nearly all of the albumin into such uncoagulable compounds. A somewhat greater quantity of acetic acid does the same, entirely preventing coagulation. We therefore feel almost certain that the carbohydrate does not originate in admixed ovomucoid, but is derived from the substance constituting the crystallized ovalbumin.

This belief is strengthened by the fact that, so far as we know, all but two of the several investigators who have thus examined coagulated egg albumin, have found evidence of the presence of considerable quantities of carbohydrates among its hydrolytic decomposition products, although most of them have endeavored to separate every trace of ovomucoid. Spencer,¹ who failed to find carbohydrate, boiled his coagulated albumin for several hours with weak potash and then for thirty minutes with 10 per cent. potash, a procedure which might lead to the destruction of carbohydrate. Moerner² who also found no carbohydrate, gives no account of the method he used in preparing the ovalbumin.

Hammarsten regards crystallized ovalbumin as a glycoprotein and considers the carbohydrate group to be a constituent of a non-proteid substance combined with the protein substance proper.

¹ *Ztschr. physiol. Chem.*, 24, 354.

² *Centrbl. Physiol.*, 7.

This is certainly true of the nucleoproteid of the pancreas from which Bang obtained guanylic acid, which on hydrolysis yielded about 30 per cent. of carbohydrate. The mucins also appear to be compounds of protein matter with sugar-yielding substances.

We have stated our belief that crystallized ovalbumin is a compound of some acid with protein substance and consider it quite probable that this acid contains the carbohydrate group.

We have been unable to obtain any evidence of carbohydrate in edestin, the crystallized globulin of hemp-seed, nor, according to Hammarsten, can a carbohydrate be split from casein, vitellin, myosin, and fibrinogen. This subject requires further careful study before a definite conclusion can be reached. At present the preponderance of evidence indicates that the carbohydrate is not derived from the protein molecule, but from substances combined with the protein as it is obtained from the tissues or secretions.

Conalbumin.—Our fractions of the proteids of egg white obtained after separating the crystallized fractions, all have a higher rotation and sulphur content and a lower temperature of coagulation than ovalbumin, as is shown in Table I. In Table III we showed that these fractions could be separated into two products by heating their solutions to 65°, filtering off the coagulum, and then heating the filtrate to 90°. In the filtrate from this latter coagulum a substance remained which was not coagulated by boiling.

The body coagulating at the lower temperature we designate *conalbumin*, on account of its close relation in properties and composition to ovalbumin. What this relation may be, we have not determined. Conalbumin and ovalbumin may be different compounds of the same protein, or the former may be a derivative of the latter involving a molecular change.

COMPOSITION OF COAGULATED CONALBUMIN.

	D.3.1.		F.3.1.		K.3.1.		Average.
	I.	II.	I.	II.	I.	II.	
Carbon	52.17	52.20	52.47	52.14	52.25
Hydrogen ...	6.98	6.70	7.02	7.09	6.99
Nitrogen	16.04	16.16	16.03	16.15	16.16	16.11
Sulphur	1.67	1.73	1.71	1.70
Oxygen	23.14	22.64	22.95
	<hr/> 100.00				<hr/> 100.00		<hr/> 100.00

These figures show very little difference in composition between ovalbumin and conalbumin, the carbon being about 0.5 per cent. lower, the nitrogen about 0.53 per cent. and the sulphur 0.08 per cent. higher.

It is possible that the higher sulphur is due to a little ovomucoid carried down with the coagulum, but this is hardly probable, as the ovalbumin coagulated in the filtrates from these preparations contained 1.61 per cent. of sulphur, which is exactly the quantity found in the most thoroughly purified preparations of ovalbumin.

Temperature of Coagulation.—When a solution of conalbumin is heated sufficiently, a finely divided flocculent coagulum separates which is very different from the dense masses that form in a similar solution of ovalbumin. As we could not separate the conalbumin from the other associated proteids except by coagulation, the temperature of coagulation of this albumin could not be determined under definite conditions. The temperature at which this substance begins to coagulate is influenced by the proportion of salts present. From a solution containing 10 per cent. of sodium chloride it separates at a lower temperature than from solutions in pure water. From the former solutions it apparently separated completely below 60°, whereas from the latter it is impossible to separate it from the ovalbumin because the latter begins to coagulate before the separation of the conalbumin is complete.

From solutions containing 10 per cent. of sodium chloride the preparations D.3.1 and K.3.1 separated below 60°, the solutions becoming turbid at about 55°. When 2.5 per cent. of K.3, D.3, and F.3 were each dissolved in 10 per cent. brine their solutions became turbid at 57°, 52°, and 58°, and flocks separated at 58°, 55°, and 59°, respectively.

Specific Rotation.—This we were unable to determine directly but indirectly the following results were obtained: of F.1, 1.5 grams were dissolved in 10 per cent. brine, the solution heated to 65°, and the coagulum filtered out and washed. The filtrate was heated to 98° and the coagulum also filtered out and washed. The nitrogen was then determined in each coagulum and in the final filtrate, and the proportion of conalbumin, calculated on the dry preparation, was found to be 25 per cent; of ovalbumin

62.7 per cent; and of ovomucoid 12.2 per cent. Subtracting the amount of rotation due to the sums of the two latter from the total rotation of F.1, we found the amount of rotation caused by the 25 per cent. of conalbumin, which for 100 per cent. was equal to $[\alpha]_D - 39^\circ$.

In the same way we found F.3 to contain 36.6 per cent. of conalbumin, 39.7 per cent. of ovalbumin, and 23.7 per cent. of ovomucoid, from which we calculated for the conalbumin $[\alpha]_D - 36^\circ$. F.2.a contained 30.9 per cent. conalbumin, 48.9 per cent. ovalbumin, and 20.4 per cent. ovomucoid, so that in this preparation we found $[\alpha]_D$ equal to $-36^\circ 21'$.

Of course such determinations cannot be accepted as final but they are sufficiently accurate to show that conalbumin has a different specific rotation from ovalbumin and is therefore a different substance. This conalbumin appears to be identical with albumin II, described by Pañormoff,¹ but so far as we can infer from this abstract of his original paper² the substance which he describes under this designation corresponds very closely with our fractions C.3, D.1, D.2, and D.3, whose mean rotation and other properties are the same as those given for albumin II.

These fractions we have shown to be mixtures of ovalbumin, conalbumin, and ovomucoid.

Ovomucoid.—After separating all the proteids coagulable by heat, Neumeister³ found in the white of eggs a substance which he called pseudopeptone. Later Mörner⁴ showed this to be a glycoproteid and named it ovomucoid, under which name it is now generally known.

In Table I it is to be noticed that all the fractions following those of the crystallized ovalbumin show an increasing value for $[\alpha]_D$ and proportional thereto an increasingly greater content of sulphur. This is chiefly due to ovomucoid associated with these fractions. In connection with the detection of sugar in the albumin molecule, it is important to recognize the difficulty with which ovomucoid can be separated from ovalbumin by fractional precipitation with ammonium sulphate.

As we have just shown, fraction F.1 contained 12.2 per cent.,

¹ *Chem. Centrbl.*, 11, 487 (1898).

² *Jour. russ. phys. chem. Ges.*, 30, 302.

³ *Ztschr. Biol.*, N. F., 9, 369 (1890).

⁴ *Ztschr. physiol. Chem.*, 18, 525 (1893).

F.3, 23.7 per cent., and F.2.a, 20.4 per cent. of ovomucoid. These fractions were obtained from those immediately following the separation of the crystalline ovalbumin, and F.1 was precipitated by simply adding an equal volume of saturated ammonium sulphate solution to the solution of these fractions.

We have obtained two preparations of ovomucoid in sufficient quantity for analysis and have found them, when dried at 110° , to have the following composition, which agrees with that given by Zanetti¹ and by Mörner².

COMPOSITION OF OVOMUCOID.

	E.4	D.3.3.	Zanetti. ¹		Mörner. ²
Carbon	49.02	48.90	48.94	48.75
Hydrogen	6.45	6.61	6.94	6.90
Nitrogen	12.71	22.16	12.46	12.65
Sulphur	2.38	2.34	2.22	2.20
Oxygen	29.44	29.99	29.44
	100.00	100.00	100.00		

The specific rotation was found to be E.4, $-61^{\circ} 38'$; D.3.3, $-61^{\circ} 10'$; F.3.3, $-61^{\circ} 20'$; K.3.3, $-61^{\circ} 30'$.

NOTE.

The Employment of Ammonium Molybdate as a Test for Tin.
—In the April number of this Journal there is a note by Mr. Allen Rogers on the use of ammonium molybdate as "a very delicate test for tin." Mr. Rogers does not refer to my paper on this subject in the *Chemical News* for December 15 last,³ and I shall therefore assume that he has not seen it. Perhaps I may therefore be permitted to state briefly the substance of that paper.

Although the color reaction involved is a well-known test for molybdenum, I have been unable to find that, prior to the appearance of my paper, it had ever been suggested as a test for tin; and, having regard to its extreme delicacy in this respect, it seems highly improbable if it had been, that the fact would have been allowed to go into oblivion. My own experience, and I

¹ *Ann. di Chim. e Farmac.*, No. 12, 1897.

² *Zeit. physiol. Chem.*, 18, 525.

³ *Chem. News*, 79, 282 (1899).

believe that of others also, is that the detection of tin in complex mixtures is, with the methods of the text-books, a great difficulty to students, whereas the test now proposed makes it exceedingly easy—assuming ordinary care to be taken.

For the success of this method, two important points must be attended to: *First*, in reducing stannic chloride to stannous chloride, the zinc employed must be entirely free from traces of tin. Samples of commercial zinc that I tried were found quite useless for the purpose. I employed pure zinc supplied by Harrington's for my experiments. *Second*, since a very dilute stannous solution, on exposure to air, becomes oxidized to stannic in a marvelously short time, as soon as the zinc and tin are completely dissolved in hydrochloric acid and the solution is diluted, the ammonium molybdate must be added at once.

I observe that Mr. Rogers finds that "a solution of stannic chloride containing 0.0000042 gram to 1 cc. gives a faint blue color with ammonium molybdate." This corresponds to 1 part of stannous chloride in rather less than 240,000 parts of solution. Had he used boiled water in making up his solution, he would have found that the delicacy of the test is far greater than this. By taking the precautions described in my paper, I was enabled to get a delicacy of 1 in 1,500,000. I concluded, however, that under ordinary conditions of working, a very distinct blue color is given by the presence of 1 part of stannous chloride in anything up to 100,000 parts of solution.

I am very glad to find that Mr. Rogers confirms my experience in three points: (1) that ammonium molybdate is a much better reagent than mercuric chloride for stannous chloride; (2) that the reagent must not be added without first of all diluting the hydrochloric acid present in the solution to be examined; and (3) that the ordinary laboratory reagent gives results that are most satisfactory.

I shall merely add that the method has been used in this laboratory during the past five months with uniform success.

J. P. LONGSTAFF.

CHEMICAL LABORATORY. UNIVERSITY OF EDINBURGH, May 22, 1900.

NEW BOOKS.

RÉPERTOIRE GÉNÉRAL, OU DICTIONNAIRE MÉTHODIQUE DE BIBLIOGRAPHIE DES INDUSTRIES TINCTORIALES ET DES INDUSTRIES ANNEXES DEPUIS LES ORIGINES JUSQU' A LA FIN DE L'ANNÉE, 1896. Technologie et Chimie. Par Jules Garçon. Tome I. Paris: Gauthier-Villars. 1900. 74 pp. Premier Fascicule.

This dictionary of the bibliography of the dyeing industries and allied subjects, is one of the most important pieces of bibliographical work that has ever been attempted for the use and convenience of chemists and technologists. It originated with the chemical section of the Société Industrielle de Mulhouse in 1892, and, after a labor of five years, the finished work was submitted to the society in 1897, when, after careful examination at the hands of a commission of experts, it was awarded the Daniel Dollfus grand prize of 5,000 francs and a medal of honor. The magnitude of this piece of bibliography will be understood when we state that the author makes reference to some 2,000 distinct works and to 110 periodicals, which latter make up about 5,000 volumes more. The first part of Vol. I, at present under notice, is devoted to the introduction, outlining the scope of the work and giving a list of the bibliographic sources availed of, both official publications and records and general and special bibliographical publications and catalogues; an alphabetical list of subject-headings under which the material is arranged; and a list of the periodicals from which the references are taken. The second part of Vol. I will be devoted to the indices of authors cited and subjects treated, while Vols. II and III will be the reference dictionary proper arranged under the various subject-headings. The scheme seems, on examination, to be a very complete one and the part of the work now in hand promises well for the way in which it will be executed.

The first part of Volume I has been issued, as just noticed, and the second part of the volume is stated to be now in press; Volume II is ready for distribution and Volume III is promised by the end of 1900.

S. P. SADTLER.

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THE CHEMISTRY OF CORN OIL.

BY HERMANN T. VULTE AND HARRIET WINFIELD GIBSON.

Received May 7, 1900.

DETERMINATION OF THE CONSTANTS.

THE samples of corn oil, the determination of whose constants has been reported in the present article, are here designated as Nos. I, II, and III.

Oil No. I is a commercial article, bought of a reputable dealer and intended for use in the manufacture of cheap paints. It has been kept in a corked tin can for six to seven years. It is of a bright, golden yellow color, is free from foots, and has a pronounced grain-like odor.

Oil No. II is a sample freshly prepared by hydraulic pressure and is of undoubted purity. Its color is somewhat lighter and its grain-like odor more marked than that of oil No. I.

Oil No. III is a product of the mash of distilleries. It is golden brown in color and from ten to twelve years old. The properties of this oil have been so affected by the process of manufacture that it is practically distinct from the other samples examined. For this reason and because this method of manufacture is now obsolete, its examination was dropped at an early stage.

DETERMINATION OF PHYSICAL CONSTANTS.

A. Specific Gravity.

Both the Sprengel tube and the Westphal balance were used in making this determination, although but little reliance can be placed on the latter beyond the second place of decimals.

Results Obtained :

OIL No. I.

	Wt. water 15.5° C. Grams.	Wt. oil 15.5° C. Grams.	Wt. oil at 100° C. Grams.	Sp. gr. 15.5° C.	Sp. gr. 100° C.
1	1.5265	1.4068	1.3315	0.9216	0.8722
2	1.6404	1.5113	1.4297	0.9213	0.8715
3	1.3602	1.2528	1.1848	0.9210	0.8710
Average for Sprengel tube.....				0.9213	0.8716
Westphal balance.....				0.921	0.895

OIL No. II.

1	2.0130	1.8547	1.7554	0.92136	0.87203
2	2.1788	2.0072	1.8958	0.92124	0.87011
Average for Sprengel tube.....				0.9213	0.87107
Westphal balance.....				0.921

OIL No. III.¹

1	1.0037	0.9288	0.8789	0.9253	0.8746
2	1.5718	1.4551	1.3780	0.9257	0.8767
Average for Sprengel tube.....				0.9255	0.8756
Westphal balance.....				0.9255

Comparison with Results of Other Observers.

Sp. gr. at 15° C.	Observer.	Reference.
0.8360	Rokitiński ²	<i>Ph. Russ.</i> (1894), 712-713.
0.9160	Curtmann	<i>Chem. Centrbl.</i> , 59, 1193.
0.9170	Bowers ²	<i>Pharm. J.</i> , Nov., 1889.
0.9200	Shuttleworth	<i>Pharm. J.</i> , 16, 1095.
0.9215	Schaedler	<i>J. Soc. Chem. Ind.</i> , 11, 504.
0.9216	Procter	<i>J. Soc. Chem. Ind.</i> , 17, 11.
0.9215-0.9244	De Negri and Fabris	<i>Ztschr. anal. Chem.</i> , 33, 547-72.
0.9220	Trimble	<i>Am. J. Pharm.</i> , 58, 265.
0.9239	Hart ²	<i>Chem. Ztg.</i> , 17, 1522.
0.9238-0.9262	Hopkins	<i>This Journal</i> , Dec., 1898.
0.9243	Dulière	<i>J. Pharm.</i> (1897), 217.
0.9244	Smith	<i>J. Soc. Chem. Ind.</i> , 11, 504-5.
0.9245	DeNegri ²	<i>Chem. Ztg.</i> , 22, 961-976.
0.9262	Mills	<i>J. Soc. Chem. Ind.</i> , 11, 504-5.

¹ Fifteen-year-old sample of oil from mash of distillery.² Petroleum ether extract.³ Dark brown oil.

B. Viscosity.

This determination was made by means of a Boverton-Redwood viscosimeter and the instrument standardized for both distilled water and rape oil at 20° C.

Results Obtained:

	Temperature.	Av. time of flow. Seconds.	Viscos. water.	Viscos. water.
Distilled water.....	20°	39	1.00
Rape oil.....	20°	405.5	100.00
Oil No. I.....	20°	283.7	9.79	70.42
Oil No. II.....	20°	297.7	10.27	73.89

Comparison with Results of Other Observers:

Temperature.	Viscos. water.	Viscos. rape.	Observer.	Reference.
18° C.-19° C	61.1	Smith	<i>J. Soc. Chem. Ind.</i> , 11, 504.
15° C.	19.2	...	Andés	" <i>Veg. Fats and Oils.</i> "
Viscosity of almond oil			Shuttleworth	<i>Pharm. J.</i> , 16, 1095.
Viscosity greater than olive			Bowers	<i>Pharm. J.</i> , Nov., 1889.

C. Index of Refraction.

The instrument used for this determination was Abbé's refractometer.

Results Obtained:

OIL No. I.		
	Temperature.	T.
1	15° C.	1.4768
2	15° C.	1.4766
3	20° C.	1.4762
4	20° C.	1.4760
Average for	15° C.	1.4767
Average for	20° C.	1.4761

OIL No. II.		
1	15° C.	1.4765
2	15° C.	1.4766
3	15° C.	1.4767
Average for	15° C.	1.4766

OIL No. III.		
1.....	19.5° C.	1.4767
2.....	20° C.	1.4766
3.....	20.5° C.	1.4764
Average for.....	20° C.	1.4765

Comparison with Results of Other Observers :

Temperature.	Refractive index.	Observer.	Reference.
15° C.	1.4765	Proctor	<i>J. Soc. Chem. Ind.</i> , 17, 11.

DETERMINATION OF CHEMICAL CONSTANTS—QUANTITATIVE.

A. Free Acid.

The method given in Allen's "Commercial Organic Analysis," II (I), 104, was used in this determination, substituting a mixture of 9 parts neutral alcohol and 1 part ether for the methylated spirit. The percentage of free acid was calculated to oleic acid.

Results Obtained :

OIL No. I.

	Wt. oil. Grams.	Vol. N/10 KOH. cc.	Acid value.	Free acid. Per cent.	Degrees acidity.
1	10.6617	7.0	3.68	1.851	6.56
2	7.2552	4.8	3.71	1.851	6.62
Average.....			3.70	1.851	6.59

OIL No. II.

1	9.9294	4.0	2.26	1.136	4.03
2	13.0816	5.2	2.23	1.121	3.97
Average.....			2.25	1.128	4.00

OIL No. III.

1	4.2351	15.6	20.64	10.387	36.83
2	6.2726	23.1	20.66	10.385	36.83
Average.....			20.65	10.386	36.83

Comparison with Results of Other Observers :

Free acid. Per cent.	Observer.	Reference.
0.75	Hart	<i>Chem. Ztg.</i> , 17, 1522.
0.88	Lloyd	<i>Chem. Centrbl.</i> , 59, 257.
0.00	Spüller	<i>Ding. poly. J.</i> , 264, 626.
5.65	De Negri	<i>Chem. Ztg.</i> , 22, 961-976.

*B. Iodine Absorption Hübl Figure.**Necessary Solutions.—*

1. HgCl₂ in 95 per cent. alcohol, 60 grams per liter.
2. Iodine in 95 per cent. alcohol, 50 grams per liter.

The alcohol used was purified by oxidation with potassium permanganate and subsequent distillation over calcium carbonate. The distillate was rejected until no discoloration was

shown on heating a small portion with a lump of solid potash for ten minutes.

3. N/10 sodium thiosulphate.
4. Twenty per cent. solution of potassium iodide in distilled water.
5. Solution of boiled starch as indicator.

Process.—Thin Erlenmeyer flasks, having accurately fitted ground-glass stoppers and flaring mouths, thus forming a gutter between flask and stopper, were used for this operation.

Equal parts of solutions 1 and 2 were mixed twenty-four hours before each test and allowed to stand in the dark until needed. About 0.250 gram oil was weighed into a test flask, the oil dissolved in 10 cc. chloroform, and 25 cc. of the mixed Hübl solution added. The excess of Hübl solution was afterward found to be about 100 per cent. The flask was then stoppered, the gutter filled with potassium iodide solution, and the whole set away in the dark for twenty-four hours. A blank was run for every determination.

After twenty-four hours the stopper was removed, sufficient potassium iodide solution added to the contents of the flask to prevent any precipitation of mercuric iodide and enough distilled water to make the bulk convenient for titration. The liquid was then titrated with N/10 sodium thiosulphate, starch indicator.

Results Obtained:

OIL No. I.

	Wt. oil. Gram.	Vol. hypo. cc.	Wt. iodine. Gram.	Iodine absorption Per cent.
1.....	0.1986	18.9	0.235323	118.44
2.....	0.2466	23.7	0.295088	119.66
3.....	0.2677	26.0	0.323725	120.90
4.....	0.22835	22.0	0.273921	119.95
Average Hübl figure.....				119.74

OIL No. II.

	Wt. oil. Gram.	Vol. hypo. cc.	Wt. iodine. Gram.	Iodine absorption Per cent.
1.....	0.2708	26.2	0.322183	118.97
2.....	0.2441	23.3	0.290108	118.85
3.....	0.2697	25.7	0.319990	118.65
4.....	0.3070	29.1	0.326232	118.02
Average Hübl figure.....				118.62

OIL No. III.				
	Wt. oil. Gram.	Vol. hypo. cc.	Wt. iodine. Gram.	Iodine absorption. Per cent.
1.....	0.2199	20.1	0.250264	113.80
2.....	0.2894	26.2	0.326215	112.72
3.....	0.2559	23.4	0.291352	113.85
4.....	0.2453	22.2	0.276471	112.70
Average Hübl figure.....				113.27

Comparison with Results of Other Observers :

Hübl figure.	Observer.	Reference.
75.8	Rokitianski	<i>Ph. Russ.</i> (1894), 712-713.
111.2-123	De Negri and Fabris	<i>Ztschr. anal. Chem.</i> , 33, 547-72.
115.17	De Negri	<i>Chem. Ztg.</i> , 22, 961-976.
116.3	Smetham	<i>Analyst</i> , 18, 191-193.
117	Hart	<i>Chem. Ztg.</i> , 17, 1522.
119.6	Hazura	<i>Ztschr. angew. Chem.</i> (1888), 696.
119.4-119.9	Spüller	<i>Ding. poly. J.</i> , 264, 626.
121.7-122.7	Lane	<i>J. Chem. Soc.</i> (1893), A, 153.
122	Hehner	<i>J. Soc. Chem. Ind.</i> , 16, 87.
122	Wallenstein	<i>Chem. Ztg.</i> (1894), 18, (ii), 119.
121.5-123.1	Hopkins	<i>This Journal</i> , Dec., 1898.
122.55	Dulière	<i>J. Pharm.</i> (1897), 217.
122.9	Mills	<i>J. Soc. Chem. Ind.</i> , 11, 504.

C. Saponification Value (Koettstorfer Figure).

The method here employed was that given in Allen's "Commercial Organic Analysis," II (I), 56-57. The alcohol employed was prepared as described under "Iodine Values," and a blank run side by side with the test for each determination.

Results Obtained :

OIL No. I.					
	Wt. oil. Grams.	Vol. N/HCl. cc.	Koettstorfer fig.	Sapon. equiv.	Ether value.
1.....	2.0127	6.95	193.71	289.61	190.01
2.....	2.5187	8.60	191.55	292.88	187.85
3.....	2.4600	8.45	192.70	291.13	189.00
Average			192.65	291.21	188.95

OIL No. II.					
	Wt. oil. Grams.	Vol. N/HCl. cc.	Koettstorfer fig.	Sapon. equiv.	Ether value.
1.....	3.8356	13.20	193.07	290.57	190.82
2.....	5.2317	18.05	193.55	289.85	191.30
3.....	2.5611	8.75	191.31	293.24	189.06
Average			192.64	291.22	190.39

OIL No. III.					
	Wt. oil. Grams.	Vol. N/HCl. cc.	Koettstorfer fig.	Sapon. equiv.	Ether value.
1.....	1.9700	6.75	190.29	294.81	169.64
2.....	2.2206	7.65	193.26	290.28	172.61
Average			191.78	292.55	171.13

Comparison with Results of Other Observers :

Koettstorfer fig.	Sapon. equiv.	Observer.	Reference.
182.81	306.9	De Negri	<i>Chem. Ztg.</i> , 22, 961-976.
188.1-189.2	298.3-296.6	Spüller	<i>Ding. poly. J.</i> , 264, 626.
188-193	298.4-290.7	De Negri and Fabris	<i>Ztschr. anal. Chem.</i> , 33, 547.
189.5	296	Hart	<i>Chem. Ztg.</i> , 17, 1522.
193.4	290.07	Mills	<i>J. Soc. Chem. Ind.</i> , 11, 504.
198.5	282.6	Smetham	<i>Anal.</i> , 18, 191-193.
198.8-203	282.2-276.4	Dulière	<i>J. Pharm.</i> (1897), 217.

D. Insoluble Fatty Acids (Hehner Figure).

From 2 to 4 grams of oil were dissolved in ether in a beaker. Fifty cc. of alcoholic potash (made by dissolving about 20 grams potassium hydroxide in 500 cc. purified and redistilled 95 per cent. alcohol) were added to the ethereal solution and the whole heated on a water-bath until saponification was effected. The liquid was then diluted with hot distilled water and heated until the ether and alcohol were entirely expelled. The aqueous soap solution thus formed was broken up with dilute hydrochloric acid and heating continued until the insoluble fatty acids formed a clear oily layer.

The fatty acids were then washed with boiling distilled water until the filtrate was neutral to methyl orange. An unusual amount of washing was found necessary with this oil, owing to the large proportion of an acid difficultly soluble in hot water. About 1500 cc. of wash-water were used and, as will be seen by the results, the amount of insoluble acids found to be unusually low.

Results Obtained :

OIL No. I.

	Wt. oil taken. Grams.	Wt. insol. fatty acids. Grams.	Hehner value.
1.....	4.6700	4.3256	92.63
2.....	2.6092	2.4121	92.45
3.....	2.3161	2.1609	93.29
Average Hehner value.....			92.79

OIL No. II.

	Wt. oil taken. Grams.	Wt. insol. fatty acids. Grams.	Hehner value.
1.....	3.5853	3.2678	91.14
2.....	3.2331	3.0142	93.23
3.....	2.6079	2.4079	92.33
Average Hehner value.....			92.23

OIL, No. III.

	Wt. oil taken. Grams.	Wt. insol. fatty acids. Grams.	Hehner value.
1.....	3.9832	3.5102	88.12
2.....	2.8297	2.4995	88.30
Average Hehner value.....			88.21

Comparison with Results of Other Observers :

Hehner value.	Observer.	Reference.
93.40	Hoppe-Seyler	<i>Bull. Soc. Chim.</i> (1866), [2], 6, 342.
93.57	Hopkins	This Journal, Dec., 1898.
94.70	Spüller	<i>Ding. poly. J.</i> , 264, 626.
95.70	Hart	<i>Chem. Ztg.</i> , 17, 1522.
96.70	Lloyd	<i>Chem. Centrbl.</i> , 59, 1193.

E. Volatile Acids (Reichert Figure).

Precisely 2.5 grams oil were saponified as in the Koettstorfer process, evaporating off the alcohol completely. Fifty cc. distilled water, containing 1 cc. phenolphthalein indicator, were then added to the dried soap and the whole heated on the water-bath until the soap was completely dissolved. While still warm the aqueous soap solution was titrated with N/2 sulphuric acid, overrunning 2 cc. The total volume of liquid was now 60–65 cc. The decomposed soap solution was then slowly distilled into a similar flask, containing 50 cc of N/10 potassium hydroxide and 1 cc. phenolphthalein indicator. A large percentage of a solid fatty acid also distilled over in white flakes, but was held back by a small wetted filter, placed in the neck of the receiving flask.

When about 50 cc of the liquid in the distilling flask had gone over, 50 cc. of distilled water were added to the residue and the distillation repeated. The contents of the receiver were then titrated back with N/10 hydrochloric acid and the "Reichert figure" calculated from the amount of volatile acids thus recovered from the two distillations.

Results Obtained:

OIL, No. I.

	Vol. N/10 HCl.	Reichert figure.	Wt. KOH for 100 g. oil. Gram.
1	45.8	4.2	0.94248
2	45.6	4.4	0.98736
Average.....			0.96492

OIL, No. II.

1	46.0	4.0	0.89760
2	45.6	4.4	0.98736
Average.....			0.94248

OIL No. III.

	Vol. N/10 HCl.	Reichert figure.	Wt. KOH for 100 g. oil. Grams.
1	39.9	10.1	2.26644
2	40.3	9.7	2.17668
Average.....		9.9	2.22156

Comparison with Results of Other Observers :

Reichert value.	Observer.	Reference.
0.33	Spüller	Ding. <i>poly. J.</i> , 264, 626.
2.5 ¹	Smith	<i>J. Soc. Chem. Ind.</i> , 11, 504.
6.7 ²	Morse	<i>N. H. Expt. Sta. Bull.</i> (1892), 16, 19.
0.0	Hopkins	This Journal, Dec., 1898.

F. Acetyl Value.

The method used was that given in Allen's "Commercial Organic Analysis," II (I), 64-65, the "Filtration Process" being the one employed.

Results Obtained :

OIL No. I.

	Wt. oil. Grams.	Vol. N/HCl. cc.	Koettstorfer fig.	Vol. N/10 KOH. cc.	Acetyl value.
1	2.3420	8.8	210.8	4.5	10.78
2	2.0092	7.6	212.2	4.1	11.45
Average			211.5	..	11.12

OIL No. II.

	Wt. oil. Grams.	Vol. N/HCl. cc.	Koettstorfer fig.	Vol. N/10 KOH. cc.	Acetyl value.
1	1.8641	7.1	213.7	3.7	11.14
2	1.4686	5.5	210.1	3.1	11.84
Average			211.9	..	11.49

Comparison with Results of Other Observers :

Koettstorfer fig.	Acetyl value (filtr.).	Observer.	Reference.
201.5	8.25	Lewkowitsch	Allen's "Com. Org. Anal.," Vol. II, 68.
200.9	7.90	Lewkowitsch	Allen's "Com. Org. Anal.," Vol. II, 68.

G. Glycerol.

Hehner's dichromate method, as given in Allen's "Commercial Organic Analysis," II (I), 316-317, was employed for this determination.

Results Obtained :

OIL No. I.

	Wt. oil. Grams.	Vol. K ₂ Cr ₂ O ₇ . cc.	Wt. glycerol. Grams.	Glycerol. Per cent.
1	2.6092	27.57	0.276395	10.59
2	2.3361	24.46	0.245217	10.50
Average				10.545

¹ Calculated. 100 parts oil require 0.56 part KOH.

² Calculated. Reported as 3.2 per cent. volatile acids.

OIL No. II.				
	Wt. oil. Grams.	Vol. $K_2Cr_2O_7$. cc.	Wt. glycerol. Grams.	Glycerol. Per cent.
I.....	2.5701	26.37	0.264359	10.29
2.....	2.0425	21.21	0.212635	10.41
Average				10.35

H. Phytosterol.

The process of Foster and Reichelmann, as given in the *Analyst* (1897), 131, was employed in this determination. The crude phytosterol, resulting from the evaporation of the ethereal extract, was estimated as unsaponifiable matter.

Results Obtained:

	Wt. oil. Grams.	Wt. ether residue. Gram.	Unsap. matter. Per cent.
Oil No. I.....	55.3945	0.7691	1.39
Oil No. II.....	49.1123	0.7036	1.43
Average			1.41

Comparison with Results of Other Observers:

Unsap. matter. Per cent.	Observer.	Reference.
1.35	Spüller	Ding. poly. J., 264, 626.
1.55	Hart	Chem. Ztg., 17, 1522.
2.86	Hopkins	This Journal, Dec., 1898.

DETERMINATION OF CHEMICAL CONSTANTS—MISCELLANEOUS.

A. Color Reactions with Sulphuric Acid.

I. Heidenreich's Test.—Two drops concentrated sulphuric acid were allowed to fall into the center of 20 drops of oil on a watch-glass. The oil and acid were then stirred together with a glass rod.

Before stirring, all three oils gave a rayed ring of mahogany-red on golden brown background.

After stirring, oils I and II gave a dark red-brown, while oil III gave a dull claret, all of honey-like consistency.

II. Carbon Disulphide Test.—One drop concentrated sulphuric acid was added to a solution of a few drops of oil in carbon disulphide; the mixture was well shaken and allowed to stand.

All three oils gave a fine violet after twenty-four hours.

B. Color Reactions with Nitric Acid.

I. Hauchecorne's Test.—From 3 to 5 parts oil by volume were shaken with 1 part nitric acid (sp. gr. 1.32). The mixture was then

heated on the water-bath for five minutes and allowed to stand.

Oils I and II gave an orange-yellow oily layer of consistency of thick honey.

Oil III gave a mahogany-red layer of much less viscosity.

II. Massie's Test.—Three parts oil by volume were shaken with 1 part nitric acid (sp. gr. 1.42) for two minutes and allowed to stand.

Oils I and II gave a bright mahogany-red oily layer of great viscosity.

Oil III gave a dark, reddish brown layer of less viscosity.

Comparison with Results of Other Observers :

HNO ₃ .	H ₂ SO ₄ .	Observer.	Reference.
Yellow-orange	Dulière	<i>J. Pharm.</i> (1897), 217.
.....	Dark red	Hart	<i>Chem. Ztg.</i> , 17, 1522.
Reddish (Massie)	Black-brown	Shuttleworth	<i>Pharm. J.</i> , 16, 1095.
Reddish yellow	Green	Brannt	"An. and Veg. Fats and Oils."

C. Silver Nitrate Reduction Tests.

I. Becchi's Test—Process of Pearmain and Moor.—Ten cc. of oil were shaken with 2 cc. of a reagent prepared by dissolving 1 gram silver nitrate in 100 cc. 95 per cent. alcohol, then adding 20 cc. ether and 1 drop of nitric acid. The mixture was then placed in boiling water for ten minutes.

All three oils gave a dark brown coloration.

II. Brullé's Test.—Twelve cc. of oil were shaken with 5 cc. of a solution prepared by dissolving 2.5 grams silver nitrate in 100 cc. of 95 per cent. alcohol. The mixture was then heated in boiling water twenty minutes.

All three oils were colored intensely black.

Comparison with Results of Other Observers :

Becchi.	Brullé.	Observer.	Reference.
Slightly darkened	Hart	<i>Chem. Ztg.</i> , 17, 1522.
Faint brown	Black	De Negri	<i>Chem. Ztg.</i> , 22, 961-976.

D. Elaidin Reaction (Poutel's Method).

One cc. of mercury was dissolved in 12 cc. of cold nitric acid (sp. gr. 1.42); 2 cc. of the freshly prepared green solution were added to 50 cc. of oil contained in a wide-mouthed, stoppered bottle, the contents of the bottle violently shaken and the agitation

repeated every ten minutes for two hours. The oil was then allowed to stand undisturbed in a warm room.

Results Obtained.—All three oils.

After two hours, orange-yellow deposit, pasty in consistency and small in amount. Orange-red, viscous liquid above.

After two weeks, little change except in gradual darkening of color and decrease in viscosity of supernatant liquid.

Comparison with Results of Other Observers:

Result of test.	Observer.	Reference.
Pasty or buttery mass	Smith	<i>J. Soc. Chem. Ind.</i> , 11, 504.
Orange-yellow color; partial solidification.	Shuttleworth	<i>Pharm. J.</i> , 16, 1095.
Orange-yellow; no solidification.	Dulière	<i>J. Pharm.</i> (1897), 217.
Much olein; between olive and cotton-seed oils.	Lloyd	<i>Chem. Centrbl.</i> , 59, 1193.

E. Rise in Temperature with Sulphuric Acid.

In making this determination, Archbutt's method for the Maumené, test, as given in Allen's "Commercial Organic Analysis," II (I), 76-77, was employed. The sulphuric acid used was of 1.842 sp. gr.

Results Obtained:

	Initial temp.	Av. rise in temp.	Specific temp.
Distilled water.....	23° C.	42° C.	100
Oil No. I.....	23° C.	75° C.	178.6
Oil No. II.....	23° C.	74° C.	176.2

Comparison with Results of Other Observers:

Maumené figure.	Observer.	Reference.
56° C.	Spüller	<i>Ding. poly. J.</i> , 264, 626.
60.5° C.	Hart	<i>Chem. Ztg.</i> , 17, 1522.
79° C.	Jean ¹	<i>J. Soc. Chem. Ind.</i> , 11, 504.
84° C.-89° C.	De Negri and Fabris ²	<i>Ztschr. anal. Chem.</i> , 33, 547-72.
89° C.	Mills ³	<i>J. Soc. Chem. Ind.</i> , 11, 504-5.

F. Heat of Bromination.

The process of Hehner and Mitchell, as given in Allen's "Commercial Organic Analysis," II (I), 80, was followed in making this determination. Six readings were taken for each sample. The calculated iodine value was found by multiplying the bromine thermal value by 5.5.

¹ Obtained by use of Jean's thermelaeometer.

² 15 grams oil + 5 cc. H₂SO₄.

Results Obtained :

	Br. Therm. Val.	Hübl No.	Calc. I. No.
Oil No. I	21.9° C.	119.74	120.45
Oil No. II	21.8° C.	118.62	119.90

Comparison with Results of Other Observers :

Br. Therm. Val.	Calc. I. No.	Observer.	Reference.
21.5	118.25	Hehner	<i>J. Soc. Chem. Ind.</i> , 16, 87.

G. Solubility in Glacial Acetic Acid (Valenta's Test).

In this determination the method of Allen's "Commercial Organic Analysis," II (I), 40, was followed. Three cc. of oil and of acid were employed.

Results Obtained :

Oil No. I.—	74° C., average of six tests.
Oil No. II.—	80° C., average of five tests.
Oil No. III.—	44° C., average of five tests.

Comparison with Results of Other Observers :

Turbidity temp.	Observer.	Reference.
65° C.	De Negri	<i>Chem. Ztg.</i> , 22, 961-976.

H. Oxygen Absorption (Livache Test).

Finely divided lead powder was obtained by precipitating metallic lead from lead acetate by means of zinc, washing the precipitate rapidly with water, alcohol, and ether, in the order named, and drying it in a desiccator.

Approximately 1 gram of lead powder, prepared as above, was spread in a thin layer on a large watch-glass and a few drops of oil added by means of a pipette, care being taken to keep the drops of oil separate. The amount of oil taken was accurately determined and was not allowed to exceed 0.6 gram. The watch-glass was then exposed to light but protected from dust and allowed to remain, at the ordinary temperature, until it ceased to gain in weight. All samples tested were examined at the same time and under the same conditions.

¹ Obtained by the use of Jean's thermelaeometer.

Results Obtained:

OIL No. I.			
Wt. oil. Gram.	Total gain. Gram.	Time required. Days.	Gain. Per cent.
0.5193	0.0310	7	5.97
OIL No. II.			
0.3313	0.0172	10	5.19

SUMMARY.

TABLE OF PHYSICAL CONSTANTS.

		Oil No. II.	Oil No. I.	Oil No. III.	Insol. fat acids.
Specific gravity.....	15.5° C.	0.9213	0.9213	0.9255
Specific gravity.....	100° C.	0.8711	0.8716	0.8756	0.8529
Viscosity (water)	20° C.	10.57	9.79
Viscosity (rape)	20° C.	73.89	70.42
Index of refraction..	15° C.	1.4766	1.4767
Index of refraction..	20° C.	1.4761	1.4765
Melting-point	22.4° C.

TABLE OF CHEMICAL CONSTANTS—QUANTITATIVE.

	Oil No. II.	Oil No. I.	Oil No. III.	Insol. fat acids.
Per cent. ash	0.065	0.0655
Acid value.....	2.25	3.70	20.65
Per cent. free acid	1.128	1.851	10.386
Degrees acidity	4.00	6.59	36.83
Per cent. iodine absorption..	118.62	119.74	113.27	120.98
Koettstorfer figure	192.64	192.65	191.78	199.15
Saponification equivalent....	291.22	291.21	292.55	281.72
Ether value.....	190.39	188.95	171.13
Hehner value.....	92.23	92.79	88.21
Reichert figure.....	4.2	4.3	9.9
Wt. KOH per 100 grams oil..	0.94248 g	0.96492 g	2.22156 g
Koettstorfer of acetic oil....	211.9	211.5
Acetyl value.....	11.49	11.12
Per cent. glycerol.....	10.35	10.545
Per cent. unsaponifiable matter	1.43	1.39

TABLE OF CHEMICAL CONSTANTS—MISCELLANEOUS.

	Oil No. II.	Oil No. I.	Oil No. III.	Insoluble fat acids.
Heidenreich— H_2SO_4	Mahogany-red to dark red-brown	Mahogany-red to dark red-brown	Mahogany to claret
Carbon disulphide— H_2SO_4	Golden brown; violet after 24 hours.	Claret; violet after 24 hours.	Claret; violet in 24 hours.
Hauchecorne— HNO_3	Orange-yellow	Orange-yellow	Mahogany
Massie— HNO_3	Mahogany-red	Mahogany-red	Dark red-brown
Becchi— $AgNO_3$	Dark brown	Dark brown	Dark brown
Brüllé— $AgNO_3$	Black	Black	Black
Elaidin test	Orange-yellow deposit; red liquid	Orange-yellow deposit; red liquid	Orange solid; dark red liquid
Maumené—Rise in temp.	74° C.	75° C.
Maumené—Specific temp.	176.2	178.6
Bromine thermal value	21.8° C.	21.9° C.	21.6° C.
Valenta's test	80° C.	74° C.	65° C.
Livache test—Per cent. gain	5.19 in 10 days	5.97 in 7 days.

APPARATUS FOR THE DETERMINATION OF AMMONIA IN WATER, BY THE WANKLYN METHOD, AND TOTAL NITROGEN BY THE KJELDAHL METHOD.

BY ROBERT SPURR WESTON.

Received June 12, 1900.

THE introduction of the ammonia method by Wanklyn¹ in 1867 has been followed by many modifications of the original apparatus. Like modifications have followed the introduction of the method introduced by Kjeldahl² in 1883.

Wanklyn originally used a tubulated retort and a Liebig condenser. The copper condenser contained a glass tube 90 cm. long and 3 cm. in diameter, thus allowing the beak of the retort to enter the condenser tube. The joint was made by wrapping a little writing paper around the beak of the retort where it entered the condenser tube. Such an apparatus is friable and unhandy.

This single still has been improved upon by various analysts, until there are several forms in use which satisfy most requirements.

An excellent form is described by Cairns³ and consists of a 2 liter, glass stoppered flask with a side-neck tube. The tube is bent so as to point vertically downward at a convenient distance from the flask. A copper condenser carrying a block-tin zigzag is attached to the neck of the flask by a rubber tube, and the lower end of the condenser is arched upward to prevent the condensed atmospheric moisture from contaminating the distillate. Leffmann⁴ makes use of a tubulated retort with a bent neck, connected with a spiral glass worm.

Perhaps the most durable and, all things considered, most convenient form of single still is the one designed by Dr. A. H. Gill and used for several years by Mrs. E. H. Richards in the laboratory of the Massachusetts Board of Health.

This still consists of a flask holding about 1300 cc., which is closed by a cork carrying a $\frac{3}{8}$ inch glass tube. This glass tube is bent so as to enter a $\frac{1}{4}$ inch straight block-tin condenser

¹ Wanklyn: "Water Analysis," 1868.

² *Ztschr. anal. Chem.*, 23, 357.

³ "Quantitative Analysis," New York, 1896, p. 271.

⁴ Leffmann: "Examination of Water," Philadelphia, 1895.

tube. The joint between the glass and tin tubes is made with a cork which is bored half way on one side to receive the glass, and half way on the other side to receive the tin tube. A rubber collar is slipped on to the lower end of the condenser tube to prevent the contamination of the distillate. The condenser is perpendicular and the neck of the flask makes an angle of 45° with it.

This apparatus has many advantages. It is easily boiled clean. Breakage of parts is not frequent, and the broken parts themselves can be replaced at a small cost. The inclined flask is also a decided advantage when the contents have a tendency to bump.

When many stills are used at once, however, these single stills are not so convenient. They take up much bench room unnecessarily, and when the condenser tubes are run through a common cooling tank, the distilling and receiving vessels are on opposite sides and are therefore somewhat inconveniently placed. Perhaps the best arrangement in using a common condenser is that described by Mason.¹

For the determination of nitrogen according to the Kjeldahl method, many forms of still have been introduced. It has been desirable from the beginning, however, to arrange groups of stills. Two forms are in general use.

At the Halle Agricultural Experiment Station an apparatus² is used which makes use of an air condenser, but the general arrangement of parts is similar to that used by Mason for water analysis, though Erlenmeyer flasks are used for distilling- and receiving-vessels.

The most important improvements in the construction of sets of stills were made by the chemists of the United States Department of Agriculture, and are described by Professor S. W. Johnson in Bulletin No. 10 of the Division of Chemistry.

This apparatus,³ of course, is well known and possesses the advantage that it can be operated from one side of the condenser tank. The distilling flasks are raised above the bench so that it is possible to reach under them for the purpose of attending to the receiving flasks. The distilling flasks are supported upon

¹ "Water Analysis," New York, 1899.

² Wiley: "Agricultural Analysis," Vol. II, 203.

³ *J. Anal. Chem.*, 4, 179; also Wiley: *loc. cit.*, 208.

an iron shelf. They are joined to the helical block-tin condenser tubes by a safety bulb and rubber connectors. This apparatus was adapted to water analysis by Hazen and Clark.¹

This apparatus was further improved by the chemists of the Massachusetts Board of Health by bringing the condensing tubes out above the open top of the condenser tank, and by connecting them directly with the stoppers of the distilling flasks, thus avoiding a rubber connection between the distilling flask and the condenser tube. This apparatus was used by the writer for several years, and was found to be quite convenient; nevertheless, some improvements suggested themselves during that time, and in designing a group of ten stills the form described below was developed.

The distilling flasks of the Johnson apparatus are supported on an iron distilling shelf, and the burners are supported on another shelf placed beneath. The metal shelves are hard to keep clean and are, of course, non-adjustable. The distilling flasks, moreover, are placed vertically, and the contents are more liable to be projected into the condenser on that account than if they are inclined. The condenser is unnecessarily large, and the receiving tubes are placed so far under the apparatus as to be inconvenient to tend.

The apparatus described below was designed to overcome the faults of the older apparatus. The drawing on page 470 shows the construction quite plainly. Any desired number of stills can be provided for.

CONDENSER TANK.

The condenser tank is built of copper or galvanized iron. The galvanized iron should be japanned. It is inclined so as to bring the lower ends well forward, and is 7.2 inches in length for each unit. The tank is 3.5 inches thick, and is rhomboidal in section, with sides 25 inches and 4.25 inches long respectively. The condenser tubes are of block tin $\frac{3}{8}$ inches in diameter and about 36 inches long. They are straight, not helical. They are soldered into the bottom of the condenser tank, projecting 2 inches below the bottom of the same. They are not supported

¹ Report of Massachusetts Board of Health on "Purification of Water and Sewage," 1890, p. 710.

except at the bottom of the tank, and are sufficiently pliant to allow connection with the flasks to be made with ease.

A swinging gutter is attached to the bottom of the condenser. This gutter can be swung under the condenser tubes when "boiling out" the apparatus. A small upturned gutter is fashioned around the bottom of the tank to catch any possible condensation. The inclined tank brings the tubes well within reach. The tank is supported by legs to the bench and by lugs to the wall.

DISTILLING STAND.

The whole system of flasks and burners is supported by means of a cross bar resting on two or more posts. The $\frac{3}{4}$ inch square, iron cross bar is drilled with holes $7\frac{1}{4}$ inches apart, and $\frac{3}{8}$ inch rods, 10 inches long, are driven into the holes. These rods project 6 inches above and 4 inches below the cross bar. Double clamps hold the rods for the burners and the 5 inch retort stand rings. The base of a Bunsen burner (E and A side lighting) is unscrewed and the burner itself is fitted with a $\frac{3}{8}$ inch rod. The above arrangement permits the flask and the burner to be moved (within limits) in any direction and at will. The flasks are supported by rings of asbestos ($\frac{1}{8}$ inch thick, $6\frac{1}{4}$ inches outside diameter, and $4\frac{1}{2}$ inches inside diameter); these asbestos rings in turn are supported by the iron rings, being secured to the latter by wires. This furnishes a very neat and springy support for the flasks, and one which, to a great extent, relieves the jar due to bumping and the consequent breaking of flasks. A water supply is provided for the condenser, entering near its bottom at one end and wasting near its top at the opposite end. All parts of the apparatus are accessible, and the flasks can be connected and disconnected with one hand, the spring of the condenser tubes helping to hold the stoppers in place.

The gas pipe is supported on the backs of the wooden posts and $\frac{3}{8}$ inch hose cocks are placed to the right of each still support; these cocks are connected with the burners by lead or rubber tubes. Either antimony rubber or selected cork stoppers can be used, the latter, perhaps, to be preferred. The ends of the condenser tube pass directly through the stoppers. If desirable, copper flasks can be used. The writer prefers to use the standard 1-liter, Jena glass round-bottomed flask.

For the determination of nitrogen by the Kjeldahl method it is best to connect the ends of the condenser tubes with glass tubes, the latter to dip into standard acid contained in the receiving vessels. Safety bulbs may also be placed at the tops of the distilling flasks connecting the same with the condenser tubes.

The first set of stills of this design was built for the laboratory of the Cincinnati Water Commission in 1898. It consisted of 10 units. Since that time three other sets have been built, all of which give satisfaction.

To determine the free and albuminoid ammonia in sands and in sewage, it has been found most convenient to place them in a 250 cc. Kjeldahl flask, and to pass through them, by means of a glass tube which should extend nearly to the bottom of the flask, steam from ammonia-free water. This ammonia-free steam is best generated in a closed copper vessel placed at one side of the condenser tank and heated by a large burner. The steam is conducted along the top of the condenser in a $\frac{3}{8}$ inch metal pipe. At suitable intervals $\frac{1}{4}$ inch tees with metal cocks are placed, from which steam can be taken for sand and sewage work.

If desirable, the burners can be easily removed and smaller rings can be used to support the Kjeldahl flasks.

Reagents are added to the flasks by means of a long-stemmed funnel.

A PROCESS FOR THE DETERMINATION OF CARBON DIOXIDE IN CARBONATES.

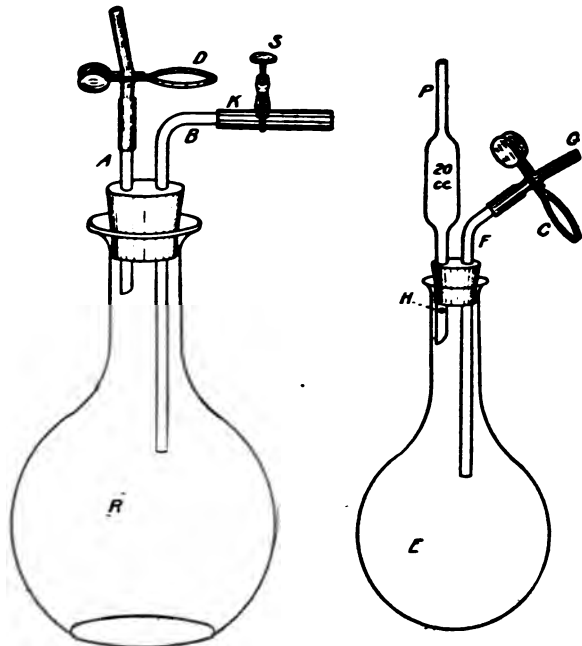
BY R. E. DIVINE.

Received May 28, 1900.

THIS process is based on the principle of Pettenkofer's process; namely, absorption of the carbon dioxide by a measured amount of standard baryta water (solution of barium hydroxide), and titration of the excess of the latter with a standard acid. The apparatus about to be described is simple in construction and may be assembled from materials available in almost every laboratory, and the process, if carried out with a reasonable amount of care, should yield fairly accurate results with anyone. It does not require the time and experience necessary in order to obtain good results by the ordinary gravimetric method.

The apparatus consists of a round-bottomed evolution flask E of about 300 cc. capacity, fitted with a rubber stopper and two tubes P and F, and as a receiving flask a 1 quart Bunsen filtering flask R fitted with two tubes A and B.

P is a 20 cc. pipette cut off so as to leave about 3 inches on each side of the bulb. The lower end is ground to a point on an ordinary grindstone, and at about 1 inch above the point there is



a small hole, H, blown into the side of the tube which enables the condensed drops of liquid to fall freely from the end.

F is a tube bent sufficiently to clear the bulb on P, projecting lower into the flask than P, and fitted on the upper end with a short piece of rubber tube G and a pinch-cock C.

The tube B of the receiving flask is fitted with a piece of heavy pressure tubing K, and a screw-cock S. Tube A is fitted with a short piece of soft tubing and a pinch-cock D.

The empty receiving flask R is first placed on a steam-bath in a place free from draughts and steam generated in a small flask or can (I use an ether can) is passed through A until the flask

is hot, and steam issues through B quite freely. S is now closed tightly, then D, and the apparatus disconnected from the source of steam and placed where it may cool. The evolution flask is now connected with the source of steam at G, and, after the air is expelled and steam issues strongly through P, the rubber tube K of the receiving flask is forced on P, then C is closed and the source of steam disconnected; the apparatus after a minute's cooling is ready to receive the carbonate. This is introduced by placing a small cut-off funnel in the end of G, washing 1 gram of the finely pulverized carbonate into the funnel, then by cautiously opening the pinch-cock C, the carbonate may be completely washed into the flask.

The screw-cock S is now opened wide. Twenty-five cc. of 10 per cent. sulphuric acid¹ are now allowed to flow on the carbonate and E is then heated over a low flame to boiling and boiled until the tube G which has been collapsed by the external pressure swells out nearly to normal size. S is then closed tightly and the heat removed. During the boiling E is allowed to hang supported only by the heavy tube K of the receiving flask. This tends to lessen in great measure the force of bumping in E which takes place as soon as the carbon dioxide is nearly boiled out of the liquid. The boiling must, however, be continued for some time in order to completely displace the carbon dioxide in E by aqueous vapor; E is now disconnected from R at K, and after three or four minutes' cooling 500 cc. of the standard baryta water are allowed to flow into R. This is accomplished without contact with the carbon dioxide of the air in the following manner: An ordinary graduated half-liter flask is fitted with a rubber stopper having three holes. Through one of these passes a tube to the bottom of the flask after the manner of a wash-bottle but fitting closely to the flask so as to remove the contents completely. Through another hole passes loosely a short tube connecting with a wash-bottle containing strong caustic potash solution for washing the air admitted to the flask. Through the remaining hole passes a short tube connecting by means of a long rubber tube fitted with a pinch-cock with a bottle of distilled water on a shelf. The standard baryta solution is of

¹ If the substance forms insoluble sulphates use tartaric acid.

such a strength that 500 cc. require 48 to 50 cc. of half-normal hydrochloric acid for neutralization.

The stopper and tubes are first removed from the measuring flask which is filled with air free from carbon dioxide, and it is then quickly filled to the mark by the siphon on the stock baryta bottle. The stopper is then replaced and the siphon of the measuring flask connected with K of the receiving flask. By opening the screw-cock S the baryta water flows into R. S is closed as the last drops enter the siphon of the measuring flask, the tube connecting with the wash-bottle pulled out of the stopper, and 20 cc. or 30 cc. of distilled water allowed to flow into the flask. This is then sucked over after replacing the wash-bottle connection, and then 20 or 30 cc. more distilled water sucked over in like manner, taking care that not much air enters R which is now shaken thoroughly; and after a minute or two washed air is allowed to enter. The flask is then shaken occasionally for about ten minutes, then air allowed to enter, disconnected from the measuring apparatus, the tubes and stopper rinsed quickly with the jet of distilled water and then immediately titrated with half-normal hydrochloric acid with phenolphthalein as indicator. The acid must not be run in too quickly and the contents of the flask must be thoroughly agitated while the acid is run in so as to avoid decomposition of barium carbonate with loss of carbon dioxide and consequent lowering of the result. The whole process including the standardizing of the baryta solution, weighing the carbonate, etc., can be quite expeditiously carried out and the results are as accurate as those of most technical processes. In working with C. P. sodium carbonate, I have obtained the following figures: 41.33, 41.42, 41.51, 41.32, 41.37, 41.34, and 41.36 per cent. Theory requires 41.51 per cent. Some trials with barium carbonate gave 21.99, 22.05, 21.98, and 21.91 per cent. Theory requires 22.33 per cent.; the barium carbonate contained quite a little chlorine. In this case tartaric acid was used to decompose the carbonate.

Freshly precipitated barium carbonate is sufficiently soluble to give a very faint alkaline reaction to the liquid, and this must be borne in mind if the color returns faintly after titrating.

BUFFALO, May 25, 1900.

[A CONTRIBUTION FROM THE LABORATORY OF THE OMEGA PORTLAND CEMENT CO., JONESVILLE, MICH.]

A METHOD FOR THE RAPID GRAVIMETRIC ESTIMATION OF LIME.

BY W. H. HESS.

Received May 26, 1900.

AN accurate gravimetric determination of lime in cement materials is very important as a check on the calcimeter. The method whereby lime is precipitated as the oxalate, ignited and weighed as the oxide, is both tedious and uncertain since prolonged ignition at a very high temperature is required to completely remove all the carbon dioxide.

The following method of estimation in which the lime is weighed as the sulphate has been found to be rapid and accurate.

The lime in the sample is precipitated and separated as the oxalate in the usual way, and the ignition is carried to the point of removing the filter from the residue of lime. The crucible is allowed to cool partially, when a portion of chemically pure dry ammonium nitrate, approximately equal in bulk to the lime in the crucible, and about twice as much chemically pure fused ammonium sulphate are added. A tight fitting cover is now placed on the platinum crucible and then gentle heat is applied. It has been found very convenient to incline the crucible at an angle of about 30° , allowing the tip of the crucible cover to project outward and then apply the flame to the tip of the cover, gradually bringing the flame under the crucible as the reaction grows less and less violent. The reaction is complete when fumes of ammonia salts are no longer driven off. Intense ignition is unnecessary and is to be avoided. The crucible should be weighed with its cover.

It was found that if ammonium sulphate alone was used, the transposition of carbonate to sulphate of lime was not always complete on first treatment. By the use of ammonium nitrate, easily fusible nitrate of lime is first formed, which is then completely transposed to the sulphate. The ammonium nitrate also helps to complete the ignition of the filter if any remains unburned.

Results on known samples of pure calcium carbonate are as follows :

Weight of CaCO_3 taken. Grams.	Weight of CaCO_3 recovered. Grams.
0.5003	0.4998
0.4997	0.4993
0.5012	0.5007
0.8472	0.8465
1.0037	1.0026

**ON A SYSTEM OF INDEXING CHEMICAL LITERATURE;
ADOPTED BY THE CLASSIFICATION DIVISION
OF THE U. S. PATENT OFFICE.¹**

BY EDWIN A. HILL.

Received May 12, 1900.

IN the following paper I will endeavor to describe the system of indexing or digesting chemical literature and patents, now in use in the Classification Division of the United States Patent Office. This division was organized about a year ago to perfect the existing classification of United States patents. Under our laws, no valid patent can be granted for any new process, composition of matter, or chemical body, described in any printed publication prior to the inventor's discovery thereof, or more than two years prior to the date of his application for such patent; and, among other things, this division is now preparing an index or digest of literature and patents relating to chemical bodies and processes, for the use of the office in making its examinations of pending applications.

The system adopted is in the nature of a reference index rather than a classification, and is one elaborated by myself, some five or more years since for another purpose, and on which we have been at work since last summer. I may add that our work was well advanced before my attention was called to the fact that there are great similarities between this system and that of Richter.

Generally speaking, in any comparison of digests or indexes that system may be considered best which, in the simplest, most certain, and most direct manner, puts the inquirer in possession of the desired information.

¹ Read before the Washington Section of the American Chemical Society, May 10, 1900.

If chemical bodies each had but one instead of many names, and if, in chemical literature, one never met with bodies as yet unchristened, then undoubtedly, the dictionary plan, pure and simple, in which the names of bodies were alphabetically arranged and the references to literature and patents were collected under their proper titles, would answer every requirement, and would be, in fact, the only proper system to use.

Practically however, most bodies known to chemists have more than one name, many have several, and the names approved in prior decades are generally not the names in highest repute to-day; nor is it likely that the names now in use will in all, or even in most cases, remain those approved in future years.

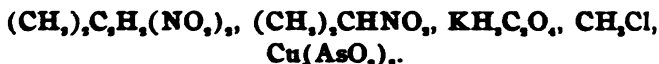
Where a chemical compound has several names, were it possible to decide now (which perhaps might be done) which one of them was, on good scientific grounds, the most appropriate in view of present knowledge, and further (which, of course, could not be done), could one be assured that such name would remain the approved name for all future time, such title could, without hesitation, be now adopted as the indexing title, under which all references to literature or patents could be entered, and all other titles and names cross-referenced into it; but, while this might be done now in certain cases, who can guarantee that all the names approved to-day shall retain that approbation as our knowledge of chemical constitution is increased?

Evidently the dictionary plan, unmodified, is not the best, and some better system must be devised not open to these objections.

It would seem that the kind and number of the component atoms of a chemical compound are its most unvarying characteristics, and are subject only to the errors of chemical analysis; and that therefore, these must form the most stable basis for any general scheme for the indexing or digesting of chemical literature; and this conclusion appears to have been independently reached by others than myself; as, for example, by Richter in his recent and former work, and by Jacobsen and Stelzner, following Richter in the index numbers of *Berichte* for 1898 and 1899. We differ chiefly in the methods by which this principle receives practical application.

The simplest, most certain, and most direct system would be to recast the empirical formulas of the compounds, writing

the atoms in the alphabetical order of their chemical symbols, and to then arrange the formulas on an alphabetical basis. For example, take the bodies



Rewriting them as above, and arranging them alphabetically, we have



It should be noted, however, that the compounds containing C and H, and broadly included in the domain of organic chemistry, constitute so large and important a class that we are fully justified in departing slightly from the alphabetical arrangement of chemical symbols, in order to thereby bring more closely together in the index bodies more or less closely related.

Generally speaking, an attempt to combine a dictionary or digest with a classification will be disastrous. We cannot sit on two stools at once, we will surely fall between them; and too much classification grafted on the dictionary or digest idea will give what is neither a good digest nor a good classification.

Classification, as applied to chemical compounds, should be supplementary to, and independent of, a mere digest or reference index.

In practice, therefore, I have modified the purely alphabetical scheme, and have adopted the following general rule for indexing:

Reject the water of crystallization, and rewrite the empirical formula in the alphabetical order of the chemical symbols, except that in carbon compounds write C first and H second; follow this rewritten formula with the constitutional formula, when given, adding the water of crystallization, if any, but arrange the titles alphabetically by the rewritten formula.

The reason for disregarding water of crystallization may be illustrated as follows: the three bodies, Na_2SO_4 or anhydrous sodium sulphate, $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ or Glauber's salt, and the heptahydrated salt $\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$, are in this way all indexed under the same indexing formula $\text{Na}_2\text{O}_4\text{S}$, and are thereby brought closely together, as they should be, in one place in the digest. If on the other hand water of crystallization was taken

into account for indexing purposes, the corresponding indexing formulas would become $\text{Na}_2\text{O}_4\text{S}$, $\text{H}_{10}\text{Na}_2\text{O}_{11}\text{S}$, and $\text{H}_{11}\text{Na}_2\text{O}_{11}\text{S}$ respectively, and these three very closely related bodies would, in consequence, be widely separated in the digest, which result would, we think, be a very undesirable one.

Our index is being prepared on the card catalogue plan. The cards used are the regular Library Bureau standard card, No. 33, size $7\frac{1}{2}$ by $12\frac{1}{2}$ cm., or approximately 3 by 5 inches, without rulings except a single blue horizontal line, ruled $\frac{1}{4}$ of an inch below the top edge of the card.

The following is a sample set of cards as actually made out in a given instance, except in size.

ONE FORMULA CARD:

$\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$ or $(\text{CH}_3\text{CO}_2)_6\text{Fe}_2$.
 Ferric Acetate; Acetate of Iron;
 Klaproth's Iron Tincture; Tinctura
 Ferri Acetatis; Iron Tincture,
 Klaproth's.
 See A Treatise on Chemistry. By H. E.
 Roscoe and C. Schorlemmer, Vol. 3, Or-
 ganic Chemistry, Part I, Page 505.

ONE POLYMER OR MULTIPLE FORMULA CARD:

$\text{C}_6\text{H}_6\text{FeO}_6$ Polymer Class 2.
 See $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$ or $(\text{C}_6\text{H}_6\text{FeO}_6)_2$
 Ferric Acetate.

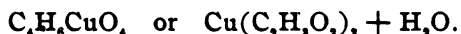
TWO CLASSIFICATION CARDS:

Acetates
 Ferric.
 See $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$ or $(\text{CH}_3\text{CO}_2)_6\text{Fe}_2$.
Iron
 Acetate of.
 See $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$ or $(\text{CH}_3\text{CO}_2)_6\text{Fe}_2$.

FOUR SUBJECT-MATTER OR TITLE CARDS:

Ferric Acetate
 See $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$.
Klaproth's Iron Tincture
 See $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$.
Iron, Klaproth's Tincture of
 See $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$.
Tinctura Ferri Acetatis
 See $\text{C}_{12}\text{H}_{18}\text{Fe}_2\text{O}_{12}$.

Considering first the formula card, it will be noted that in the formula the atoms are rearranged in the alphabetical order of their chemical symbols, except that in carbon compounds C comes first, and H second; and that, had there been water of crystallization in the formula, it would have been rejected. Then follows the constitutional formula, where the water of crystallization, if any, would appear. Thus had the body been cupric acetate, the first line of the formula card would have been



Then follows under the blue ruling, all the names given for the body in question, and finally the reference, by volume and page, to the work indexed.

When a citation is to a patent instead of to a book or other printed work, the reference given will be about like this:

See U. S. Patent No. 319082 to Fahlberg, dated June 2, 1885.

The arrangement of these cards in the card index is strictly an alphabetical one. Thus, all cards reading C, take precedence of C₁, C₂ of C₃, etc., etc. In the series C₁, etc., the order of arrangement would be:

C₁AgNO; C₁AgS; C₁Ag₂O₃; CBr; CClHgN; CCl₂O; CCl₄; CCuN; CHAgO₃; CHBr; CHCl₂I; CHCl₃; CH₂AgNO₃S; CH₂Cl₂; CH₂S; CH₂AsCl₂; CH₂Br; CH₂ClOP; CH₂F; CH₂; CH₂AsClO; CH₂CIN; CH₂AlNO₃S₂; CH₂CIN; C₂H₂; C₂H₂CaClO₂; C₂H₂AgNO; C₂H₂As; C₂H₂AgNO₃; C₂H₂O; C₂H₂Cl₂P; C₂H₂CIN₂O; C₂H₂N₂O₂S₂; CdO₂S; ClCu; ClH₂HgNO; DiN₂O₂; HKO₂S; KMnO₄; PCl₃; PCl₅, etc., etc.

The foregoing series will fully illustrate the method of arrangement.

The polymer or multiple formula cards perform the following function: There are many bodies which analysis shows to be composed of certain elements in certain proportions, but for which theory at present indicates a formula containing two, three, or more times as many atoms. Thus at one time the formula of ferric chloride was written FeCl₃, whereas it is now very often written Fe₂Cl₆, and such doubled and tripled formulas are very common.

In all cases where, in the formula as written, the exponents of

all the atoms have a common divisor, after the doubled, tripled, or other form as found is used for preparing the formula card, the formula is then reduced to its lowest terms by dividing the exponents by their greatest common divisor, and a polymer or multiple formula card, made out in the form shown by the foregoing sample ("Class 2," "Class 3," etc., on the polymer cards, indicates the common divisor). In this way the index is rendered independent of any changes in the formula consequent upon future changes of view with reference to constitutional formulas and other matters of theory.

A mere reference index or digest should in no way depend upon any theory subject to future changes with advancing knowledge. Classification, on the other hand, must necessarily depend on theory, and must change as knowledge is increased.

These polymer cards are sorted in with the regular formula cards to form part of the formula division of the index or digest. We may illustrate the function of these cards thus: suppose ferric chloride had been found in the literature under the formula Fe_2Cl_6 , and so indexed, but no polymer card made out, and some one consulted the index under the formula FeCl_3 ; the reference, though in the digest, would not be found, but with the polymer card made out the inquirer by it would be referred to the card Fe_2Cl_6 , where the required references would appear. All the remaining cards compose the subject-matter or title index, comprised first of the classification cards, second of the regular subject-matter or title cards, and third of any general topics that it may be thought advisable to include in the alphabetical division of the index.

These cards require but little explanation, except that the general statement should be made that all references to the literature or patents of chemical bodies are intended to be entered on the formula card, and all the other cards are merely used as cross references, referring the inquirer to the formula card for all required information.

Classification, it will be noted, is attempted only to a limited extent now, but will be carried out much more completely hereafter, by a supplementary scheme not yet fully perfected — independent of, though based on, the reference index.

The present scheme however, it will be observed, does inci-

dentially, bring together very many closely related carbon and other compounds, and arranges alphabetically, under such general titles as acids, alcohols, ethers, acetates, chlorides, etc., the specific bodies of the given class.

In practice, to use the digest, if the empirical formula of any compound is known, it must be rewritten by the rule already given, and at once is disclosed the definite place in the formula index where the desired references, if digested, will be found entered upon the formula card.

If on the other hand, one of the various names of the body is given, the subject-matter index is entered alphabetically, and a cross reference obtained to the rewritten formula with which the formula index is entered for the required information.

The question arises, as between this system and such a one as that adopted in the *Berichte*, which one of them is the best; that is, the most practical for the intended uses. It may be said generally that the Patent Office needs the index for exactly the same purpose as the scientific or practical chemist; *i. e.*, to obtain references to the literature concerning definite chemical bodies, where either the name or the chemical composition or both is given, so that the system best for the one use is probably also best for the other as well.

We consider our system to be preferable, certainly so at least for the patent office, and I may say that it was elaborated and adopted without any knowledge of the work of Richter as followed in the *Berichte* by Jacobsen and Stelzner.

In our system, the arrangement of the formulas is governed by the following general principles in the following order:

- 1st. The number of C atoms
 - 2nd. The number of H atoms
 - 3rd. The alphabetical arrangements of the symbols of the remaining elements (including H in other than carbon compounds).
- } in carbon compounds.

Practically, in indexing, or in using the digest as an index, the only thing to be remembered is, that in carbon compounds C comes first and H second, and that otherwise the rearrangement of formulas and the arrangement of such formulas in the digest is always alphabetically by the symbols, instead of by the names of the component elements.

That the *Berichte* system is much more complex will be seen at once. Other things being equal, we deem that system which is simplest to be the best, provided it achieves a result of equal value. The ideal system, we think, produces the best result with the minimum of labor, both mental and physical.

In rewriting the empirical formula by the *Berichte* or Richter system, one must remember the following arbitrary established order of precedence of certain of the chemical symbols; *viz.*, C, H, O, N, Cl, Br, I, F, S, P, and this both in rewriting the formulas and in entering the table. One must also consider the number of carbon atoms in the compound, the number of different varieties of atoms, and various other things as well.

Thus for example, in the Richter system, the following are the principles which govern, in the order of their relative importance :

- 1st. The number of C atoms.
- 2nd. The number of different kinds of atoms other than C.
- 3rd. The arbitrary arrangement of ten of the component elements in the following order; *viz.*, C, H, O, N, Cl, Br, I, F, S, P, all taking precedence over the remaining elements.
- 4th. The arrangement of all other component elements in the alphabetical order of their chemical symbols.
- 5th. The arrangement of chlorides, bromides, amides, anilides of carbon acids, acetyl and benzoyl derivatives, oximes, phenylhydrazones, etc., under the formulas of their corresponding bases.
- 6th. The arrangement in general, of salts, either under the formulas of their bases, or of their acids.
- 7th. The arrangement of salts of quaternary ammonia bases under the formulas of their corresponding hydroxides.

By way of comparison, I have taken from the pages of the *Berichte* index a number of bodies, with the formulas written and arranged as there shown, and have rewritten and rearranged them on our own classification division plan.

FORMULAS TAKEN FROM THE *BERICHTE* INDEX.Pages refer to *Berichte*, No. 19, of 1899.

C ₁	{	CO ₂	}	p. 3448.	C ₂	{	C ₂ HOC ₂	}	p. 3454.	C ₄	{	C ₄ H ₁₃ ON	}	p. 3466.
		CCl ₄					C ₂ H ₂ O ₂ N ₂					C ₄ H ₇ ON ₂ S		
		CS ₂					C ₂ H ₂ N ₂ Cl ₂					C ₂ H ₁₂		
		CHN					C ₂ H ₂ O ₂ Cl ₂					C ₂ H ₂ O ₂		
		CHCl ₃					C ₂ H ₂ O ₂ Br					C ₂ H ₁₁ N		
		CHBr ₃					C ₂ H ₂ O ₂ S ₂					C ₂ H ₁₄ N ₂		
		CH ₂ O					C ₂ H ₂ N ₂ Cl ₂					C ₂ H ₁₀ Cl ₂		
		CH ₂ N ₂					C ₂ H ₂ O ₂ N					C ₂ H ₁₅ O ₂ N		
		CH ₂ I ₂					C ₂ H ₂ N ₂ Cl ₂					C ₂ H ₁₅ O ₂ N		
		CH ₂ N ₂					C ₂ H ₂ O ₂ S					C ₂ H ₁₅ ON ₂ Cl ₂		
C ₁	{	CH ₂ Br		p. 3450.	C ₂	{	C ₂ H ₂ NBr	}	p. 3455.	C ₃	{	C ₃ H ₂ O ₂ Cl ₂	}	p. 3471.
		CH ₂ O ₂					C ₂ H ₂ O ₂ N					C ₃ H ₂ O ₂ Cl ₂		
		CH ₂ N					C ₂ H ₂ O ₂ S					C ₃ H ₁₄ N ₂		
		COCl ₂					C ₂ H ₂ ONBr					C ₃ H ₁₄ N ₂ Cl ₂		
		CNBr					C ₂ HO ₂ Cl ₂ Hg ₂					C ₃ H ₁₅ O ₂ N		
		CHO ₂ Cl					C ₂ H ₂					C ₃ H ₁₅ O ₂ N		
		CHNS					C ₂ H ₂ O					C ₃ H ₁₄		
		CO ₂ N ₂ Br ₂					C ₂ HO ₂ N ₂					C ₃ H ₁₆		
		CHO ₂ N ₂ Br					C ₂ H ₂ OBr					C ₃ H ₁₆		
		C ₂ H ₂					C ₂ H ₂ OCl					C ₃ H ₁₆		
C ₁	{	C ₂ Cl ₆		p. 3451.	C ₃	{	C ₃ H ₂ ON	}	p. 3459.	C ₄	{	C ₄ H ₂ O ₂	}	p. 3475.
		C ₂ Cl ₄					C ₃ H ₂ ON					C ₄ H ₂ O ₂		
		C ₂ HN ₂					C ₃ H ₂ ON					C ₄ H ₂ O ₂		
		C ₂ Cl ₆ Hg ₆					C ₃ H ₂ ON					C ₄ H ₂ O ₂		
		C ₂ I ₂ Hg ₂					C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
C ₁	{			p. 3452.	C ₃	{	C ₃ H ₂ ON	}	p. 3460.	C ₄	{	C ₄ H ₂ O ₂	}	p. 3480.
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
C ₁	{			p. 3453.	C ₃	{	C ₃ H ₂ ON	}	p. 3461.	C ₄	{	C ₄ H ₂ O ₂	}	p. 3491.
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
C ₁	{			p. 3464.	C ₃	{	C ₃ H ₂ ON	}	p. 3464.	C ₄	{	C ₄ H ₂ O ₂	}	p. 3474.
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		
							C ₃ H ₂ ON					C ₄ H ₂ O ₂		

In the foregoing arrangement, the formulas are given in the same order as in the *Berichte*, other formulas which come in between these being omitted; and in the following table these formulas are rewritten and rearranged on the plan which we have adopted, a few formulas not found in the *Berichte* index being added to illustrate the application of our scheme to inorganic bodies.

FORMULAS REWRITTEN AND ARRANGED ON THE PLAN ADOPTED BY THE CLASSIFICATION DIVISION, U. S. PATENT OFFICE.

The rewritten formula is in our digest generally followed by the empirical or constitutional formula as usually written by chemists, but from lack of space I have omitted the constitutional formula in many cases in the following table:

C ₀	Not in <i>Berichte</i> Index.	{	AgCl	}	H ₀	{	CBrN or Br CN	}	C ₁	{	CBr ₂ N ₂ O ₄ or C(NO ₂) ₂ Br ₂	}
			AgMnO ₄				CCl ₂ O or COCl ₂					
			AlH ₂ NO ₂ S ₂ or NH ₄ Al(SO ₄) ₂				CCl ₄					
			+ 12H ₂ O				CHBrN ₂ O ₄ or CHBr(NO ₂) ₂					
			AsH ₂ KO ₄ or KH ₂ AsO ₄				CHBr ₂					
			AuCl ₄ K or KA ₂ Cl ₄				CHClO ₂ or COCl.OH					
			BNaO ₂ or NaBO ₂				CHCl ₃					
			Ba ₂ N ₂ O ₆ or Ba(NO ₂) ₂				CHN or HCN					
			Br ₂ OSe or SeOBr ₂				CHNS or CN.SH					

<p>C₁ { H₁ { CH₂I, CH₂N, CH₂O or COH, H₃ { CH₂Br CH₂N₂ H₄ { CH₂O₂ CH₂N or NH₂(CH₃) H₅ { CO₂ CS₂ H₆ { C₂Cl₆ C₂Cl₄Hg₂ or C₂Hg₂Cl₆ C₂HCl₃Hg₂O₂ or CH₂Cl₂CO₂H H₁ { C₂HCl₃O or CCl₃.CHO C₂HN₃ H₂ { C₂H₂ C₂H₂CIN₃ C₂H₂N₂O₃ or C₂H₂(NO₂)₂ C₂H₂BrO₂ H₃ { C₂H₂Cl₂O₂ or CCl₂.CH(OH)₂ C₂H₂Cl₂N₂ or (CH₂Cl)₂N₂ H₄ { C₂H₂O₂S₂ or CHO.CH(SO₃H)₂ H₅ { C₂H₂Cl₂N₂ C₂H₂NO₃ or C₂H₂NO₂ C₂H₂BrN or N(CH₂)₂Br H₆ { C₂H₂O₂S or C₂H₂(SO₃H) H₇ { C₂Hg₂I₂ C₂HN₃O₂ or N = C - N - N HN - C - CO - O ≥ N H₂ { C₃H₂O or CHO.C₂H H₃ { C₃H₂BrO C₃H₂BrO H₅ { C₃H₂ClO C₃H₂N₂O₂S C₃H₂ or CH₂.CH.CH₂ C₃H₂BrNO or N.CO.C₂H₅.HBr C₃H₂N₂S C₃H₂NO or OH.CH₂.CH₂.NH.CH₃ H₆ { C₃H₂NS or CH₃ - CH - SH CH₂ - NH₂ H₁₁ { C₃H₁₁N₂O or OH(CH₂)₃N.NH₂ H₂ { C₃H₂N₂O₄ H₄ { C₄H₄O or $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{CH} - \text{CH} \end{array}$ C₁ { H₇ { C₄H₂N₂OS H₁₂ { C₄H₁₂N₂ or (CH₂)₂N.N(CH₂)₂ H₁₃ { C₄H₁₃NO or N(CH₃)₃.OH C₄Hg₄N₂</p>	<p>Not in C₀ <i>Berichte Index.</i></p> <p>C₂ { H₁ { C₃HCl₃N₄ H₂ { C₃H₂Cl₂N₄O C₃H₂Cl₄O₃ H₄ { C₃H₂O₂ H₁₁ { C₃H₁₁N H₁₃ { C₃H₁₂ or CH₂(CH₂)₃CH₃ H₁₄ { C₃H₁₄N₂ H₁₅ { C₃H₁₅NO₂ or N(CH₂)₃(C₂H₄.OH)OH H₆ { C₆Cl₆ C₆H₂Br₃NO H₂ { C₆H₂O₆ C₆H₂Cl₂O or C₆H₂Cl₄(OH) C₆H₂Cl₂N or C₆H₂Cl₄NH₂ H₅ { C₆H₂Cl₂OPS or SP(OC₄H₉)Cl₂ C₆H₂ C₆H₂Cl₆ C₆H₂N₂ or N - CH HC - C - N - CH₃ N - C - N = CH C₆H₂O₂ or C₆H₂(OH)₂ C₆H₂S or C₆H₂.SH H₁₄ { C₆H₁₄ or (CH₂)₂CH.CH(CH₂)₂ C₆H₁₁Br H₁₅ { C₆H₁₅P or P(C₂H₅)₃ H₂₀ { C₆H₂₀As₂O₂ or (CH₂)₂(OH)As₂OH(CH₂)₂ Cl { ClO₃ Cl₂Ni or NiCl₂ CoS Cr { CrO₄Pb or PbCrO₄ Cr₂K₂O₁₀S₂ or Cr₂(SO₄)₃K₂SO₄ + 24H₂O CuN₂O₆ or Cu(NO₃)₂ FeK₂O₂S₂ or FeK(SO₄)₂ H { HK₂ or K₂H H₂MoO₄ H₃N or NH₃ HgNO₃ IKO₃ or KIO₃ K₂NiO₂S₂ or NiSO₄ + K₂SO₄ + 6H₂O MoO₄Pb or PbMoO₄ Na₂O₂Si or Na₂SiO₃ OPb or PbO O { O₂Pd or PdO₂ O₂Te or TeO₃ SSi or SiS</p>
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As a practical test of the two systems, take the six following bodies; rewrite them first by our system and find them in our table; then rewrite them by the *Berichte* rules and find them in the *Berichte* table; and the demonstration of the superior simplicity of our system will be complete. The bodies are:

1. SP(OC₆H₅)Cl₂
2. C₆H₂Cl₃(OH)
3. CH₃Cl₃CO₂H
4. CN.SH
5. N.CO.C₆H₅.HBr
6.
$$\begin{array}{c} \text{N} = \text{C} - \text{N} - \text{N} \\ | \qquad \qquad \qquad \diagup \\ \text{HN} - \text{C} - \text{CO} - \text{O} \end{array}$$

This comparison speaks louder than words, and I think most chemists will agree with me that our system affords to the inquirer, with the minimum of technical knowledge, the maximum of information, in the surest manner, and with the minimum of mental and physical labor, and without the danger that a future change in theory will mislead the future user of it. In other words, the use of the digest is as far as possible independent of all theory, and founded only on unchanging facts.

Let me here call attention to the point that in the *Berichte* system the formulas of very many large classes of bodies, such as salts, amides, anilides of acids, etc., etc., have no representation in the index. Their formulas do not appear in it at all; but only their names, which are classified under the different formulas of some related body; so that in a given case, unless one remembers all these various classes of excepted bodies, if forgetting any of these things he rewrites the formula, and enters the *Berichte* digest or index with it, thus rewritten, he finds none of the matter indexed. He must first remember that the body sought is not indexed under its own, but under some different formula of a body more or less closely related to it; that is, that the body belongs in some one of these many excepted classes, and then, after determining under what base or acid it will be found, he must enter the table with the rewritten formula, not of the body itself, but of the given base acid or other body to which it is now supposed to be related, although advancing knowledge may hereafter prove this view as to supposed relationship to be erroneous.

Moreover, in the case of a body of which the number and kind of the component atoms are known, but as to the constitution of which little or nothing is known, while the body may be correctly entered in the *Berichte* index under the formula of some base or acid or other supposedly related body, it would evidently never be found, because not knowing its constitution, we do not know the base or acid under which it is indexed, and so would not find it in the table.

In our system, every chemical body indexed is represented in the digest or table by its rewritten empirical formula. No bodies are indexed as subheads under the formulas of other compounds. The indexing, and conversely, the finding of the body in the index, is rendered absolutely independent of any theories of constitution whatever, and made to depend solely on the kind and number of the component atoms, arranged alphabetically by their symbols, except that in carbon compounds, C comes first and H second. Nothing can be more simple.

No serious attempt is made, however, to make the system, which is merely intended to be a reference index, at once a classification, and also an index as well; that is, classification is not pushed beyond the point where it begins to encroach on the digest idea; and any such attempt, I believe, will surely fail to fully fulfil either function in the highest degree. In a good index, the classification idea must be kept subordinate. Hence, it follows that from our point of view, the *Berichte* system, as a mere digest or index, as well as that of Richter and all other similar systems, is inferior to ours in the points indicated; while as systems of classification, they can not but be inferior to such as are founded on proper lines. Such systems can be worked out without being hampered by the digest or dictionary idea, and which important work — classification proper as distinguished from a mere digest or index — we hope to be able to take up at some future time, on a comprehensive scale, as supplementary to the present work in hand.

It would be manifestly unfair, however, in this comparison of systems, to overlook the fact that both in the field covered, and in the intended use, the two systems are not exactly the same. Richter's system is designed for and applied solely to the bodies of organic chemistry for the use of specialists in that branch

familiar with its classification. Ours covers the entire domain of chemical research, both inorganic and organic, and is for the general inquirer. From a classification standpoint, the order of preference—C, H, O, N, Cl, Br, I, F, S, P—is justified in organic chemistry; but in inorganic chemistry it has no justification, and would lead to awkward and unfamiliar formulas, with no compensating advantages.

When a general reference index to all bodies, both organic and inorganic, is under consideration, if an order of preference is to be established, one will have to adopt different orders in the organic and inorganic domains, or else do as we have done—that is, establish no order of preference whatever, with the one exception of giving C and H preference in that order in carbon compounds so as to thereby effect a differentiation of organic from inorganic bodies.

Moreover, Richter's system is more adapted to the needs of those who are studying bodies as a class and to whom classification is of greater importance; while our system is specially adapted to the needs and requirements of those who are merely searching for references to the literature of specific chemical bodies—particularly those bodies the empirical formulas of which are known, but as to the constitution of which little if any information is at hand.

The approval of our system, therefore, does not necessarily imply that it is a criticism of or shall supersede that of Richter. Because of these differences in the field covered and in the intended use, the two systems have really no serious quarrel; and where ours is applied to organic bodies, the Richter formula could also be given on the cards prepared on our system to facilitate reference to the *Berichte*, and the Richter Lexicon, with its 75,000 titles of organic compounds.

In conclusion, there arises the question of how far the system described in this paper is adapted to the needs of chemists generally as a universal scheme for the indexing or digesting of chemical literature. That it fully meets the needs of the Patent Office we have no doubt, and for myself, I can not see why the needs of the practical and scientific chemist are not about the same as ours.

The object of a dictionary of chemistry, a reference index, or

a digest system, such as those contained in the German *Berichte* and similar works, and the *Abstracts* of the Chemical Society, is to furnish to the chemical inquirer, in the best and quickest way, digested information and references to the latest literature on any given chemical body, process, or general chemical topic. Our system directly covers, very fully, and in, we believe, the best and quickest way, the inquiry as to the chemical body, and incidentally, the inquiry as to any specific chemical process, since every such process has for its aim the production of a specific chemical body, and hence the literature relating to such process will, of course, be digested under the formula of the resulting product.

An index or digest of general chemical topics, or processes of a general nature not specially adapted to the production of a specific body, but to many bodies more or less closely related, can not, of course, be included in any mere formula scheme, which can only represent specific bodies, but must come into some general or dictionary plan based on names or titles, and such references of this class as it might seem desirable, to include in a general scheme of chemical indexing, would easily work in with the alphabetical arrangement of chemical names provided for in the system we have adopted.

Probably the most natural objection which the practical chemist would make to the adoption of the system of indexing by rewritten formulas as one of the component parts of a general scheme for chemical indexing, would be that to rewrite or rearrange the chemical symbols in the accepted formula on a purely alphabetical basis, would appear to offend the chemical sense, and do violence to the long-established usage of chemists in writing such formulas with the component elements or radicals arranged in an order depending largely on their relative, positive, or negative qualities, using these terms in their broadest chemical meaning.

In answer to this objection, it should be noted that if this really be a valid objection, it applies just as fully to the system used by Richter in the earlier editions of his "Lexicon" and adopted and approved in the *Berichte* Indexes and other publications as to ours; and it can be urged with equal force against the monumental work of Richter, just published, which is an

enlarged edition of his earlier work. So that, with such backing as Richter and the *Berichte*, it would seem as if the objection was not as valid as might at first appear.

Moreover, in our system it is an unvarying rule that the rearranged formula is never used or written, whether on cards or elsewhere, without being immediately followed by the empirical or constitutional formulas, so far as the same are known or inferred; so that an objection which might have force, were nothing but the rewritten formulas given in the digest or on the index cards, loses its force when the ordinary formula, so familiar to the chemist, is always an invariable accompaniment of the new and unfamiliar indexing formulas.

As soon as the idea is fully grasped that the rewritten formula is merely an arbitrary arrangement, in the nature of a position indicator, determining position in a mere reference index to literature and nothing more, the chemical sense will be no longer offended. The justification for its use lies in the fact that such a formula unerringly indicates one, and one only, definite and specific place in the index where we are to look for all references, with a certainty that no other character, name, or title of the body can afford. With other systems we are somewhat uncertain where to look for our information;—with this system all uncertainty at once disappears.

Personally I should be glad to see a general scheme of indexing current chemical literature carried out at some future time for the benefit of American chemists, under the auspices, for instance, of the Smithsonian Institution, along these general lines which have been blocked out in our Classification Division, modified or improved perhaps by the combined wisdom and experience of the American Chemical Society.

For example, the Smithsonian Institution might publish an annual index to current chemical literature, divided into a formula division, arranged along some such lines as here suggested, and a subject-matter or title division, in which all names and subjects were alphabetically arranged, and the names of chemical bodies all cross-referenced into the formula index, all references to the literature of chemical bodies being collated under the unvarying formula of the body, and not under one of its various and varying names.

Such an index should cover the leading chemical periodicals—such works as *Berichte* and the *Abstracts* of the Chemical Society, and the more important chemical publications of the year.

The vast army of chemical workers in our universities, laboratories, and corporate and government offices and institutions, state and national, should be enlisted in the work, each willing worker assigned some special publication or portion of same, and be supplied with standard library bureau cards and general instructions; and the cards as prepared sent in to the central bureau established here in Washington, where, after being sorted into place in the receiving cabinets, and with proper editing, they would form the basis from which would be compiled the annual index volume.

These volumes would probably be less of a digest and more of an index than the present *Abstracts* of the Chemical Society or the *Berichte*, and would cover a somewhat different field than either.

Lastly, these annual volumes should be sold at cost price, so as to become a working tool in the hands of all the chemical workers of the country.

I may here briefly refer to a special development of this work now being carried out in our Patent Office Index. We have procured two copies each of the *Berichte* Indexes for 1898 and 1899. The separate titles in the formula portion of these indexes are in most cases small enough to be cut out and pasted on our standard indexing cards and still leave room enough at the top to rewrite the formula on our own plan. We are also considering the application of this system of cutting and pasting from two duplicate copies to the new Richter "Lexicon" with its 75,000 titles, and possibly to the four volumes of the last edition of Watts' "Dictionary," Thorpe's "Dictionary of Applied Chemistry," the yearly abstract volumes of the *Journal of the London Chemical Society*, and such other works of general reference as it may be found advisable.

But to return, in conclusion, to the idea of a central bureau at Washington, supervising the indexing of chemical literature, would not some such plan, properly matured, and carried out to a successful completion, be a work worthy of the great scien-

tific institution of the national capitol, founded expressly for the dissemination of useful knowledge, and be directly in line with their publication in past years, of the indexes to the literature of specific chemical bodies, which has so much redounded to their credit? It seems to me at least that it would be a work worthy of their best endeavor, and of whose great utility there could be no question whatever.

CAUSE OF THE LOSS IN WEIGHT OF COMMERCIAL PLATINUM, WHEN HEATED UNDER SOME CONDITIONS.

BY ROBERT W. HALL.

Received June 15, 1900.

THE fact that commercial platinum sometimes loses weight when heated has been frequently noticed and experiments made to determine the cause of the loss. This loss has been observed under at least seven conditions.

1. *When platinum is made the cathode for the spark from an induction coil.*—That platinum is dissipated under this condition, was observed by Plücker¹ and very fully described by him. A. W. Wright² and others studied the same phenomena. The platinum is dissipated alike in air, in vacuum, and in hydrogen, and the phenomena are regarded as purely physical or mechanical.

2. *When platinum is heated in a Bunsen gas flame, sufficiently, reducing to deposit some carbonaceous matter on the platinum.*—Rémont³ obtained in this way, in thirty minutes, a deposit weighing 22 milligrams and containing 10 milligrams of platinum. Rémont made some experiments to show that this loss is not due to the heated carbonaceous matter alone. He attributed it to some constituent of the gas.

3. *When platinum is heated in the ordinary smokeless Bunsen flame.*—Some observers note a constant loss under these conditions. Wittstein⁴ found such a loss and attributes it to osmium, which he found in the platinum scrap of that time. Stolba⁵ found that a platinum crucible lost weight at the rate of 16 milligrams in twelve hours. Stolba remarks that while he

¹ *Ann. Phys. Chem.*, 103, 90 (1858).

² *Sill. J. Sci. and Arts*, January, 1877.

³ *Bull. Soc. Chim.*, 35, 486 (1891).

⁴ *Dingler's poly. J.*, 179, 299 (1866).

⁵ *Ibid.*, 198, 177 (1870).

does not deny the possible presence of osmium, there would have to be more osmium in the platinum than in the original ore, to account for the continuous losses he observed. Erdmann,¹ with Pettenkofer, had, however, studied the behavior of platinum crucibles in the Bunsen flame and observed the formation of a gray coating, but without loss or gain in weight. Erdmann concludes that the gray coating is due to molecular change in the platinum. Crookes² discusses Erdmann's paper and agrees with him.

The writer's experience agrees with that of Erdmann, so far as constancy of weight is concerned. Possibly some of the platinum of commerce about 1866 to 1870 differed in composition from that commonly used. It may be noted here that platinum heated in a flame of hydrogen containing arsine and then strongly ignited, shows the phenomena observed by Erdmann in a very marked degree.

4. *When platinum is very strongly heated in a furnace for firing porcelain.*—Elsner³ found that platinum burned into porcelain, was entirely dissipated when exposed to the full heat of an oven used for firing porcelain, during the burning of a batch.

Platinum black, however, placed in a small porcelain crucible, under the same conditions, only melted to small globules, with a metallic luster.

5. *When platinum is heated in a combustion tube in air.*—H. Kayser⁴ attempted to free air from possible hydrocarbons by passing it over platinum in a glass tube heated externally. He observed phenomena, which he explained by the assumption that the platinum gave up finely divided particles to the air.

6. *When platinum is heated by an electric current.*—That platinum is dissipated when heated in air by the electric current seems to have been discovered first by Thomas A. Edison.⁵

Edison observed that glass, surrounding the wire, became covered with a mirror of what he assumed to be metallic platinum and that when the wire was placed in a bulb and as

¹ *J. prakt. Chem.*, 79, 117 (1860).

² "Select Methods in Chemical Analysis," 2nd Ed., p. 681.

³ *J. prakt. Chem.*, 99, 257 (1866), from *Chem. tech. Mitth.* (Elsner) 7, 36 (1857-1858).

⁴ *Ann. Phys. Chem.*, 34 (1888).

⁵ *Chem. News*, 40, 152, from *Proc. Am. Ass.*, 1879, 173.

perfect a vacuum as possible produced, the loss ceased. Edison pronounced the action to be purely mechanical.

Nahrwold,¹ in apparent ignorance of Edison's work, repeated part of Edison's experiments and further observed that the metallic coating dissolved in aqua regia, only in part. Nahrwold pronounces no opinion as to the nature of the action.

Berliner² endeavored to explain the action. He found that platinum, which had been exposed to air, gave up gas when heated in a vacuum, that while doing so platinum was dissipated, giving a deposit on glass cylinders surrounding the metal and that the dissipation of the platinum ceased, when gas was no longer given off. In hydrogen the behavior was exactly the same as shown by a single successful experiment and Berliner, therefore, concluded that the action was a purely mechanical one caused by the escaping gases.

7. *When platinum is heated before the blast-lamp.*—Beilstein³ notes that platinum crucibles, both of pure and of less pure platinum, lost weight to an important degree on ignition but that after repeated ignition the loss became less. The writer's experience does not agree with this. For example, in a series of experiments, a crucible which had been used for some years, was ignited nineteen times, under varying conditions, with a total loss of 10.3 milligrams; on being ignited for the twentieth time (see Table B, Experiment 1) it showed a loss of 2 milligrams in thirty minutes,—a greater loss than was observed in any of the preceding experiments. Perhaps if a new crucible had been used for the first experiment of the series, results like Beilstein's, would have been obtained.

The attention of the writer was directed to the subject soon after moving to a new laboratory, by finding that the ordinary platinum crucibles of commerce lost weight so rapidly, when used for the conversion of calcium oxalate into calcium oxide, that even an approximately constant weight could not be reached.

This was the more remarkable, as the burners and general arrangements were the same, as had been used for several years,

¹ *Ann. Phys. Chem.*, 31, 467 (1887).

² *Ibid.*, 33, 287 (1888).

³ Short abstract *Chem. Centrbl.*, 1880, 614. Original in *Z. rusk. chim. obs.*, 12, 1880, not accessible.

with the exception that for a foot-blower, there was substituted a steady blast from a blowing engine, giving a more evenly high temperature.

The gas used was a mixture of retort gas and of the so-called "water-gas" enriched with naphtha gas. It contained about 15 per cent. of carbon monoxide and in this respect resembled the gas, which had been used formerly, without causing any loss of weight in the crucibles.

The loss was not due to the high temperature alone, for the writer has frequently heated crucibles with a steady blast, to the most brilliant "blue whiteness," without loss.

Experiments showed that the loss was not due to dust in the air or gas, acting as a sand-blast, for filtration of the air and gas through cotton-wool made no difference; nor to unusual amounts of the impurities removable by alkalis in the gas, for the losses still continued after a careful purification of the gas by passing it through potassium hydroxide solution and over "soda-lime."

Nor was the loss likely to be due to any peculiarity in the platinum used, for old and new crucibles of soft, comparatively pure platinum and a crucible of a platinum-iridium alloy, gave about the same results. In every case, after heating, the platinum showed a somewhat roughened surface, with a most beautiful silvery luster.

TABLE A.

Soft, commercial "pure" platinum from Eimer and Amend, New York.

No.	Weight of wire before heating.	Weight after heating.	Gas used.	Duration of experiment in minutes.	Loss or gain in milligrams.	Loss per 15 minutes.	Remarks.
1.	2.9085	2.9085	CO	30	0.0	0.00	
2.	2.9085	2.9085	"	30	0.0	0.00	
3.	2.9083	2.9080	"	35	-0.3	0.13	{ Supply of gas insufficient. Some air may have gained access. { Slight mirror on the glass. { Slight mirror on the glass. { Slight mirror on the glass.
4.	2.9080	2.9054	air	30	-2.6	1.30	
5.	2.9054	2.9022	"	30	-3.2	1.60	
6.	2.9022	2.8977	"	45	-4.5	1.50	

No.	Weight of wire before heating.	Weight after heating.	Gas used.	Duration of experiment in minutes.	Loss or gain in milligrams.	Loss per 15 minutes.	Remarks.
7.	2.8977	2.8889	air	90	-8.8	1.46	Slight mirror on the glass. Mirror. Thinner wire. Higher resistance. Current more easily regulated. Hence heat higher.
8.	1.7258	1.7137	"	60	-12.1	3.02	
9.	1.7137	1.6905	oxygen	60	-23.2	5.80	
10.	1.6905	1.6902	CO ₂	90	-0.3	0.05	Mirror. Heat not high. Difficult to regulate current owing to small resistance.
11.	2.8889	2.8716	oxygen	85	-17.3	3.05	
12.	2.8468	2.7165	"	360	-130.3	5.43	Glass covered with an almost opaque mirror.
13.	3.0935	3.0939	hydrogen	60	+0.4		Hydrogen found to contain some arsine.
14.	2.8714	2.8715	"	90	+0.1		Hydrogen free from arsine.

Some experiments were therefore undertaken to answer the question why platinum crucibles sometimes keep a constant weight, when heated in a gas flame, to a temperature very near their melting-point and why they sometimes lose weight, at a rate amounting to a milligram in fifteen minutes.

Wires of the ordinary soft "pure" platinum of commerce, about 40 cm. in length, were placed within a glass tube 78 cm. in length and 3.5 cm. in diameter, closed at each end with caoutchouc stoppers and provided with openings for the introduction and exit of the different gases used.

The platinum wires used were hung on platinum rods and these again hung on copper conducting wires. A stream of the gas used was passed through the apparatus and then the wire was brought to a temperature as near its melting-point as could be done safely, by means of an electric current.

The details of these experiments are given in table A.

The results of these experiments was unexpected.

They show that the loss of weight, in the reducing or neutral gases, carbon monoxide or carbon dioxide, is zero or very slight; that in hydrogen there is a very slight gain, while

in air and oxygen the loss is very rapid, in Experiment No. 12, amounting to 5.4 milligrams in each fifteen minutes. The two experiments with hydrogen, showing an actual gain, are not necessarily in conflict with Berliner's result, since in these two experiments the platinum was cooled in hydrogen, while in Berliner's experiment the platinum was cooled in a vacuum. The following experiments were made, however, and do seem to conflict with Berliner's result. The wires used in Experiments 13 and 14, were heated by the current, for sixty and ninety minutes, respectively, in an atmosphere of carbon dioxide. After this treatment they weighed within 0.05 milligram of the original weights; that is, the differences were within the error of weighing. It may be remarked that Berliner's experiments were qualitative, but he describes the deposit from hydrogen as an "opaque platinum mirror." Berliner's experiments were beautifully planned and no explanation of the apparent conflict suggests itself.

It, therefore, appeared probable from the result of these experiments, that a highly oxidizing gas flame would cause a greater loss of platinum, than a more reducing one.

Experiments were made to test this by placing a platinum crucible in a blast-flame, first high up in the flame, above the point where the maximum temperature could be reached and where the flame should be oxidizing and then bringing it down by steps, nearer the burner, below the zone of maximum temperature, where the flame should be more reducing, under the following conditions.

Two burners, with converging flames were used, a steady blast from a blowing engine, the flame surrounded by perforated clay crucibles, the blast adjusted in each case so as to give the maximum heat, in the particular position; duration of each experiment thirty minutes.

Weight of the platinum crucible, 11.9694 grams.

The following results were obtained:

TABLE B.

No. of Exp.	Distance between bottom of crucible and the burners. cm.	Loss of weight. Mgs.	Loss per 15 minutes. Mgs.	Remarks.
1.	15.5	2.0	1.0	{ Heat below that of four succeeding experiments.
2.	12.5	1.1	0.55	
3.	10.5	0.8	0.40	{ Good white heat. Heat higher than in No. 2.
4.	8.5	0.5	0.25	
5.	7.5	0.5	0.25	{ Heat as high as in No. 3. Heat lower than in No. 5. Seemed about the same as in No. 1.
6.	6.5	0.5	0.25	

In these experiments the loss in weight varied so much more with the position in the flame, than with the temperature, that the latter relation is entirely masked.

In all cases, where the wires lost weight, when heated by electricity in air or oxygen, mirrors were produced on the glass tube.

In Experiment No. 12, table A, the deposit was removed by aqua regia; only part of it dissolved at first in concentrated aqua regia, just as Nahrwold observed. The solution was filtered from the insoluble part, precipitated by ammonium chloride, and the precipitate ignited. The residue weighed 56.3 milligrams. The insoluble portion was ignited and found to weigh 56.4 milligrams. After ignition this residue dissolved in concentrated aqua regia. A further black precipitate was obtained from the alcoholic filtrate from the precipitation of the first aqua regia solution, which weighed 1.3 milligrams. Hence, if it is assumed that the mirror and these three fractions had about the same composition there were recovered in all 114 milligrams out of 130.3 milligrams. Some of the deposit lay on the platinum supports and could not be recovered.

The behavior of the aqua regia solutions was very different from that of 130 milligrams of the original wire.

These experiments show that the loss of weight of commercial platinum heated by the electric current or before the blast-lamp, is due to the chemical action of oxygen, that certain elements are fractioned out of the impure platinum and that the loss of weight is not, as has been suspected, due to the use of "water-

gas", except in so far as this gas is likely to give a hot and strongly oxidizing flame, when used in burners having an air supply, designed for a gas requiring more oxygen.

The behavior of platinum when heated under the last five conditions may be explained by the hypothesis that a volatile oxide of platinum is formed, stable at high and low temperatures, but unstable at intermediate temperatures, like the platinous chloride (Pt Cl_2) of Troost and Hautefeuille.¹

If, as is the case in the blast-flame, the compound is swept away or if, as in the porcelain furnace in the combustion tube and with the heated wire, there is no cooler part of the platinum, upon which the metallic product of the decomposition of the hypothetical oxide can settle, the platinum loses weight. If on the contrary the flame is a quiet one, as is the case when a crucible is heated in a Bunsen flame, and only a part of the metal is very strongly heated, the hypothetical oxide decomposes at once on emerging from the most strongly heated zone and the platinum is deposited on the cooler part of the crucible, producing the molecular change of the surface, without gain or loss of weight, noticed by Erdmann and Crookes.

It is hoped to continue this work in this laboratory, to examine the deposit, to test the behavior of purer platinum, to try to isolate the hypothetical oxide and to fix, if possible, the conditions under which commercial platinum may be heated to whiteness without loss.

LABORATORY OF ANALYTICAL CHEMISTRY,
HAVEMEYER CHEMICAL LABORATORY,
NEW YORK UNIVERSITY, June, 1900.

THE PRECIPITATION OF THE SULPHIDES OF NICKEL AND COBALT IN AN ALKALINE TARTRATE SOLUTION, TOGETHER WITH AN INVESTIGATION INTO THE NATURE OF CERTAIN TARTRATES OF THESE METALS.

By O. F. TOWER.
Received June 19, 1900.

INTRODUCTION.

VILLIERS² recommended some time ago a method for the qualitative separation of nickel and cobalt based on the action of hydrogen sulphide on an alkaline solution of the tartrates

¹ *Compt. rend.*, 84, 946 (1877).

² *Ibid.*, 119, 1263, and 120, 46 (1894-95).

of these metals. This method as commonly carried out may be stated as follows: The solution of the sulphides of nickel and cobalt in aqua regia is evaporated to expel chlorine, and after suitable dilution sufficient tartaric acid is added to prevent precipitation by sodium hydroxide. This last reagent is then added until the solution is strongly alkaline, and hydrogen sulphide run in to saturation. Cobalt sulphide is precipitated, while nickel sulphide remains in solution, imparting to the solution a dark color. When nickel is present only in very small quantities the color is brown; with larger quantities it is a jet black.

The failure of this method to give good results in the hands of students, has led to a critical investigation of it, the results of which are given in the following pages. In order to be able to approach this subject intelligently this account will be preceded by an account of an investigation into the nature of some tartrate solutions of nickel and cobalt, together with a description of any such tartrates which it has been found possible to isolate.

All substances before being analyzed were dried in an air-bath at 120°.

Nickel and cobalt were always determined electrolytically following in most respects the method of Fresenius and Bergmann,¹ which may be outlined as follows: To the solution containing nickel or cobalt, which is free from chlorides, are added 100 cc. ammonia solution (sp. gr. 0.96) and 10 cc. of a solution of ammonium sulphate (305 grams to liter). A current from two storage battery cells (3.2 volts, 0.48 ampere) was passed through the solution for from four to five hours. This length of time was found to be sufficient to effect complete precipitation of the metal (quantities not exceeding 0.1100 gram), provided tartrates were absent. It was necessary, however, to determine these metals frequently in the presence of tartrates. In such cases the amount of metal deposited at the end of four or five hours was weighed, removed from the electrode, and the apparatus then reconnected and left running all night. The results were then very satisfactory.

Potassium was determined as sulphate. After removing the nickel either by precipitation as sulphide or by electrolysis, tar-

¹ *Ztschr. anal. Chem.*, 19, 314 (1880).

taric acid was destroyed by gentle ignition, and the potassium then converted into sulphate by heating with ammonium sulphate.

TARTRATES OF NICKEL.

The effect of tartaric acid in preventing the precipitation of the hydroxides of nickel and cobalt has been known since the time of Rose,¹ and since then has been frequently discussed. The literature on the preparation of well-defined tartrates of these metals is, however, rather meagre.

That nickel tartrate cannot be precipitated from solutions of nickel salts is well known. Werther² prepared it by saturating a boiling solution of tartaric acid with freshly precipitated nickel hydroxide. The substance was thrown down as a pale green powder practically insoluble in hot or cold water, but soluble in warm alkalies. This has been essentially confirmed. The precipitate is apparently amorphous, although Werther considered it crystalline. The filtrate is still colored green, showing that precipitation is incomplete, but what is precipitated is extremely insoluble in water. The substance washed and dried at 120° yielded 28.44 per cent. nickel. The theoretical percentage of nickel in $\text{NiC}_4\text{H}_4\text{O}_6$ is 28.39. This substance dissolves readily in alkalies, only when they are present in large excess. To effect solution, considerably more potassium hydroxide is required than a quantity equivalent to the nickel tartrate; that is, more than two molecules potassium hydroxide to one nickel tartrate, and the action is greatly accelerated by heating. The behavior of this nickel tartrate toward atmospheric moisture is worthy of remark. The precipitated powder dried at 50° still contains moisture. In this condition, however, it neither deliquesces nor effloresces, the moisture content remaining constant. On the other hand no definite hydrate seems to exist, for different samples on drying at 120° were found to contain different percentages of residual water. Furthermore, the water-free substance is not in the least hygroscopic. When exposed under a bell-jar to an atmosphere saturated with moisture, it does not gain in weight more than a milligram or two in several weeks. Nickel tartrate can be made

¹ Gilbert's *Annalen*, 73, 74, foot-note (1823).

² *J. prakt. Chem.*, 38, 400 (1844).

equally well by treating a hot solution of tartaric acid with nickel carbonate.

Fresenius¹ prepared a hydrated racemate of nickel from nickel acetate and racemic acid. It resembles nickel tartrate in some of its characteristics but was not further investigated.

If freshly precipitated nickel hydroxide is treated with cold dilute tartaric acid, the nickel hydroxide dissolves, imparting to the solution a green color, probably due to the formation of nickel tartrate. On warming this solution the light green powder mentioned above precipitates. To determine the molecular size of the substance in solution, a solution was prepared by treating an excess of nickel hydroxide with a known quantity of tartaric acid, and then finding the freezing-point of the resulting solution. The reaction between nickel hydroxide and tartaric acid is very slow, so that after five days' standing free tartaric acid was still present in sufficient quantity to redden blue litmus paper, 2 or 3 milligrams of the acid being uncombined. This was not sufficient to influence materially the results which follow. The apparatus employed for the freezing-point determinations was Beckmann's improved form,² and is particularly designed to exclude moisture from the solution during the process. This is accomplished by operating the stirrer by means of an electromagnet, thereby obviating the necessity of having a hole through the stopper for the stirring shaft. Since aqueous solutions were used in these experiments, the exclusion of moisture made very little difference, but this form of apparatus has other advantages. It is exceedingly convenient, requiring the operator's attention only for a few minutes at the time of freezing, and besides the regularity of stirring insures greater accuracy. Individual determinations of the freezing-point of the same substance did not vary more than 0.002°. Five cells of a storage battery were used to supply power for the electromagnet. Table 1 gives the results with solutions of nickel tartrate prepared as indicated above. The last four are with different concentrations of the same solution. The strength of such solutions was always determined by precipitating the nickel in an aliquot portion by electrolysis.

¹ *Ann. Chem.* (Liebig), 42, 23 (1842).

² *Ztschr. phys. Chem.*, 21, 239 (1896).

TABLE I.

Amount $\text{NiC}_4\text{H}_4\text{O}_6$ in 100 cc. solution. Grams.	Depression.	Apparent Molecular weight.
1.8795	0.139°	260
1.7205	0.121°	273
0.8602	0.081°	202
0.4301	0.042°	193
0.2150	0.025°	163

Molecular weight of $\text{NiC}_4\text{H}_4\text{O}_6 = 206.8$.

In the case of the more concentrated solutions these results show the molecular weight calculated from the lowering of the freezing-point to be higher than that calculated from the formula. One would expect, however, the reverse, because of dissociation in aqueous solution. By the freezing-point method Kahlenberg has shown the apparent molecular weight of potassium tartrate in solutions of moderate strength to be about one-half that calculated from the formula, $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$.¹ These facts lead to the conclusion that nickel tartrate exists in fairly concentrated solutions largely in the form of double molecules.

Determinations of the electrical conductivity of these solutions show abnormal results also. In Table 2, m is the fraction of a gram-equivalent ($\frac{1}{2}\text{NiC}_4\text{H}_4\text{O}_6$) in a liter; L is the equivalent conductivity expressed in reciprocal ohms.²

TABLE 2.

Temperature 18°.		Temperature 25°.	
Nickel tartrate.		Magnesium tartrate. ³	
m .	L .	m .	L .
0.1664	8.29	0.03125	54.9
0.0832	9.34	0.0156	64.1
0.0416	10.8	0.0078	74.0
0.0208	18.7	0.0039	82.6
0.0104	26.5	0.0020	90.1
0.0052	36.8	0.0010	95.9
0.0026	48.8
0.0013	63.6

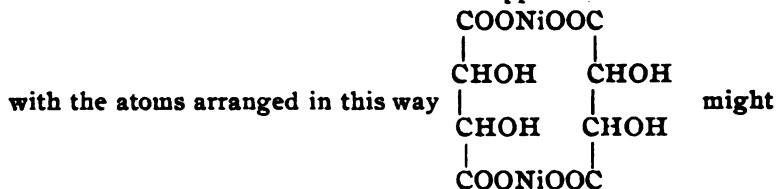
The values of the conductivity of nickel tartrate are exceptionally small, as will be seen by comparing them with the values for magnesium tartrate, which illustrate normal conduc-

¹ *Ztschr. phys. Chem.*, 17, 585 (1895).

² These units are those proposed by Kohlrausch, and fully described in "Leitvermögen der Elektrolyte," by Kohlrausch and Holborn.

³ Determinations by Walden, *Ztschr. phys. Chem.*, 1, 337 (1887), recalculated by Kohlrausch and Holborn.

tivities of tartrates of this class. The different behavior of nickel tartrate can only be ascribed to a peculiar constitution of the salt itself. It seems reasonable to suppose that a substance



well suffer less dissociation than a normal tartrate. Dissociation in concentrated solutions would probably be of the nature, Ni^{++} and $\text{C}_4\text{H}_4\text{O}_6\text{NiC}_4\text{H}_4\text{O}_6^-$. On dilution this anion itself would gradually be decomposed, so that the conductivity would not advance with the same regularity as it does in the case of simple binary electrolytes. In Table 2, the results with nickel tartrate show such behavior, as is seen by comparison with the value for magnesium tartrate. Such a formula as the above will also explain very satisfactorily the results obtained from the freezing-point method. Measurements of the electromotive forces with solutions of this kind will not be given, until the facts relating to some other tartrates of nickel have been discussed.

Fabian¹ prepared potassium nickel tartrate by allowing cream of tartar to act on nickel carbonate at a temperature of about 50°. On evaporating the solution obtained over sulphuric acid a greenish substance was deposited, which effloresced on exposure to air and was soluble in water. After drying this substance at 110° and analyzing, he obtained the following results :

	Found. Per cent.	Theory for $\text{NiK}_2\text{C}_4\text{H}_4\text{O}_{12}$. Per cent.
NiO	16.8	17.3
K ₂ O	20.9	21.7

This work has been repeated with essentially the same results. Cream of tartar was allowed to stand in contact with an excess of nickel carbonate at about 40° for some time. The green solution was filtered off, and left to evaporate over sulphuric acid. No definite crystals were obtained, neither by evaporating rapidly in a partial vacuum nor slowly in the air with a string. The residue was invariably of a scaly appearance possessing

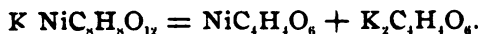
¹ *Ann. Chem.* (Liebig), 103, 248 (1857).

a very light green color. The results of the analysis of this substance are :

	Found. Per cent.	Theory for $K_2NiC_2H_4O_{12}$. Per cent.
K.....	18.21	18.06
Ni	13.38	13.55

According to Fabian, on boiling a solution of this substance a gelatinous mass separates out, which cannot be washed completely free from alkali. This has been found to be true, the precipitate being rather flocculent and of a very light green color. If, however, a solution of potassium nickel tartrate is digested for some time at about 75° , a light green pulverulent precipitate can be obtained, which was supposed to be a basic tartrate of nickel. After washing it thoroughly and drying at 120° , analysis proved it to be identical with the insoluble nickel tartrate already described, a sample yielding 28.25 per cent. nickel. On long standing this decomposition takes place gradually at lower temperatures. It is, therefore, necessary to exercise care in the preparation of potassium nickel tartrate, for, if tartaric acid is digested for a long time with nickel carbonate, some of the potassium nickel tartrate formed is apt to decompose in this manner :

Insoluble form



When the solution is filtered, the potassium tartrate passes through with the potassium nickel tartrate, and remains mixed with it on evaporation. This is revealed by the percentage of potassium being too high and that of nickel too low to correspond to the formula $K_2NiC_2H_4O_{12}$.

Determinations of the molecular weight of this substance were made by means of the freezing-point method. For this purpose different solutions were employed,—some prepared as above described, some by dissolving the solid substance in water, and others by dissolving nickel hydroxide in the proper amount of tartaric acid and adding that quantity of potassium hydroxide just sufficient to form $K_2NiC_2H_4O_{12}$. The results follow :

TABLE 3.

	Amount $K_2NiC_4H_4O_{12}$ in 100 cc. solution. Grams.	Depres- sion.	Apparent molecular weight.
Solution prepared direct from	3.764	0.434	162
$NiCO_3$ and $HKC_4H_4O_6$	1.882	0.255	140
	0.941	0.170	105
Solid substance dissolved in	3.752	0.430	165
water.....	1.876	0.253	140
Solution prepared from $Ni(OH)_2$,	3.295	0.419	153
$H_2C_4H_4O_6$ and KOH	1.6475	0.246	128
	0.8238	0.139	112
	0.4119	0.079	98

Molecular weight of $K_2NiC_4H_4O_{12}$ = 433.

It is essential to know something about the dissociation of this substance before one can judge intelligently of its true molecular size. To throw light on this subject the electrical conductivity of a solution of potassium nickel tartrate was measured. The equivalent conductivity is given on the basis of one potassium atom ($\frac{1}{2}$ molecule $K_2NiC_4H_4O_{12}$ in a liter).

TABLE 4.

Temperature 18°. Potassium nickel tartrate.		Temperature 25°. Sodium tartrate. ¹	
m.	L.	m.	L.
0.1522	74.6
0.0761	84.3
0.0381	94.2	0.03125	87.1
0.0190	101	0.0156	93.2
0.0095	114	0.0078	98.2
0.0048	124	0.0039	102.1

The conductivity of the double tartrate is increasing with the dilution much faster than that of the sodium tartrate. This is undoubtedly due to the dissociation of potassium nickel tartrate mostly into K^+ ions and $NiC_4H_4O_{12}^{--}$ ions in the more concentrated solutions. On dilution, however, the nickel also begins to dissociate from the complex anion, thus causing the rapid increase in the conductivity. For corresponding concentrations the conductivity of the double tartrate always exceeds that of the sodium tartrate.

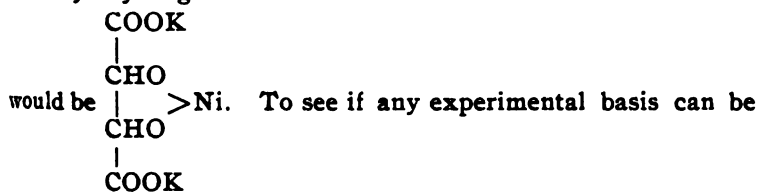
Kahlenberg,² in his article on complex tartrates of lead and

¹ The conductivity of sodium tartrate is given for comparison. The results are those of Bredig, *Ztschr. phys. Chem.*, 13, 191 (1894), recalculated by Kohlrausch and Holborn.

² *Ztschr. phys. Chem.*, 17, 577 (1895).

copper, found that these substances were probably dissociated sufficiently, so that the apparent molecular weight was about one half the true molecular weight. The solutions of potassium nickel tartrate used here were, however, a little more dilute than Kahlenberg's solutions; besides the substances are somewhat different in nature. Table 3 shows the apparent molecular weight to be only a little more than $\frac{1}{2}$ of the molecular weight of $K_2NiC_4H_4O_{12}$. This may be accounted for on two hypotheses; either the substance is in large part dissociated into K^+ , K^+ and $NiC_4H_4O_{12}^-$ ions as was indicated in connection with the conductivity measurements, or there exist separately in the solution potassium tartrate and nickel tartrate, the former dissociated, the latter, however, not. The evidence seems to favor the former of these hypotheses. For, if the second were correct, one would expect the deposit left on evaporation of the solution not to have a uniform composition. But the deposit on the side of the dish was of the same composition as that on the bottom. Furthermore, washing the deposit slightly with water had no effect on its composition. If the substance had been a mixture of potassium tartrate and nickel tartrate, this treatment would very likely dissolve more of the former salt than of the latter.

The fact that the addition of tartaric acid to solutions of nickel salts prevents the precipitation of nickel hydroxide is usually explained by the supposition that in such cases the nickel replaces the hydrogen atoms of the alcoholic hydroxyls of the tartaric acid, while the potassium takes the place of the two carboxyl hydrogen atoms. The formula of such a substance



found for this view, solutions of nickel tartrate, to which potassium hydroxide had been added, were investigated by the usual physico-chemical methods.

The freezing-point method was first employed in order to observe the effect on the size of the molecule of successive

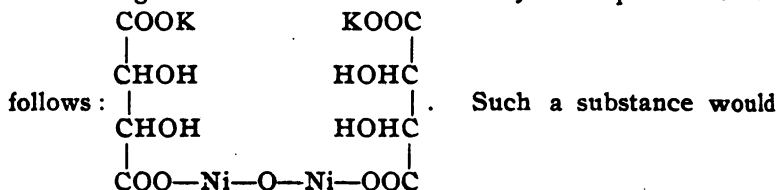
additions of potassium hydroxide¹ to a solution of nickel tartrate.

TABLE 5.

Solution containing 1.8795 grams nickel tartrate in 100 cc.

Expt. No.	KOH added to above solution. Gram.	Depression.	Remarks.
1	0.0000	0.139°	Reaction acid.
2	0.1226	0.180	Reaction alkaline.
3	0.3270	0.187	
4	0.5314	0.134	
5	0.7358	0.180	Solution jelly-like.
6	0.8175	0.156	
7	1.311	0.233	

In Experiment 7, the quantity of potassium hydroxide is just sufficient to form, with the nickel tartrate, $K_2NiC_4H_4O_6$. In the fourth the depression is a minimum, and here the amount of potassium hydroxide added is nearly one half that added in the seventh, or the ratio is about one molecule potassium hydroxide to one nickel tartrate. If the molecular weight is calculated from the depression, 0.134° , on the basis of $NiKC_4H_4O_6$ existing in solution, 299 is obtained. The molecular weight according to the above formula is in round numbers 245. This case is almost exactly parallel to the results obtained by Kahlenberg¹ with certain alkaline tartrate solutions of lead and copper. So undoubtedly the molecular size of the substance here is about twice that represented by the formula $NiKC_4H_4O_6$, and following Kahlenberg the molecular structure may be represented as



hardly be expected to dissociate so as to yield nickel ions. The evidence for such a molecular structure would, therefore, be increased, if it could be shown that no nickel ions exist in the solution.

For this purpose measurements were made of the electromotive force generated by an element with nickel electrodes, one

¹ Sodium hydroxide was also employed, but since the results are similar, only those with potassium hydroxide are given.

² *Loc cit.*

electrode being surrounded by a solution of a nickel salt of known concentration and the other surrounded by the solution in question. The electromotive force of such an element is expressed by the formula,

$$\pi = \frac{RT}{nE_0} \ln \frac{c_1}{c_2},$$

where the letters indicate the usual quantities, c_1 and c_2 being the concentration of the nickel ions in the two solutions. Evaluating the equation for $R = 8.311$ electrical units, $T = 291$ (18° C.), n , the valence of nickel = 2, $E_0 = 96,540$ coulombs, and reducing to Briggs' system of logarithms, one obtains,

$$\pi = 0.02881 \log \frac{c_1}{c_2}.$$

Measurements were made according to the Poggendorf-Ostwald method with a Lippmann capillary electrometer. The nickel solution of constant concentration was in every case a solution of nickel nitrate containing 0.1 gram-molecule in a liter. The electrodes were made by covering platinum electrodes with nickel by electrolysis. These electrodes were tested by connecting them with an electrometer, when they were dipping into the same solution of nickel nitrate. Under these conditions the electrometer reading should be zero. Few electrodes, however, could be found which would fulfil this condition. Those chosen showed potential differences of not more than 0.003 volt. Measurements were made first of the electromotive forces between the standard solution and solutions of nickel nitrate containing 0.05 and 0.01 gram-molecule in a liter, respectively, and afterwards with the solutions of nickel tartrate under consideration. In each case the electrodes were reversed and the potential difference measured again. The averages of the two readings so obtained are given in Table 6.

TABLE 6.
Temperature 18° .

No.	Between 0.1 mol. $\text{Ni}(\text{NO}_3)_2$ and	π observed. Volt.	π calculated. Volt.
1	0.05 mol. $\text{Ni}(\text{NO}_3)_2$	0.010	0.0087
2	0.01 " "	0.032	0.0288
3	0.0208 " $(\text{NiC}_2\text{H}_3\text{O}_6)_2$	0.048
4	0.0761 " $\text{NiK}_2\text{C}_8\text{H}_8\text{O}_{12}$	0.075
5	0.0572 " $\text{KC}_4\text{H}_4\text{O}_6\text{NiONiO}_6\text{H}_4\text{C}_4\text{K}_2$	0.210
6	0.0748 " $\text{K}_2\text{NiC}_4\text{H}_4\text{O}_6$	0.236

Where the concentration of the nickel ions was known the electromotive force has been calculated from the formula. The agreement is seen to be fairly good. Nos. 3 and 4 are measurements with the solutions already mentioned of nickel tartrate and potassium nickel tartrate, respectively. The potential differences show that the concentration of the nickel ions in these solutions is somewhat less than in a 0.01 mol. solution of nickel nitrate. Fewer nickel ions are present in the potassium nickel tartrate solution than in the solution of nickel tartrate, which was to be expected, for the same reason that the replaceable hydrogen atom of an acid salt is only very slightly dissociated.¹

To find the concentration of the nickel ions in solution 5, which is the one formed by adding to 100 cc. of a solution containing 18.795 grams of nickel tartrate, 0.5314 gram of potassium hydroxide,² 0.210 is substituted for π in the formula and c_1 is made equal to 0.1×0.8 , for 0.1 mol. nickel nitrate is about 80 per cent. dissociated. From this the value of c_1 is found to be $10^{-8.386}$. This shows that, relatively speaking, no nickel ions are in the solution, which is corroborative evidence of the existence of the molecular structure ascribed to this substance on page 510.

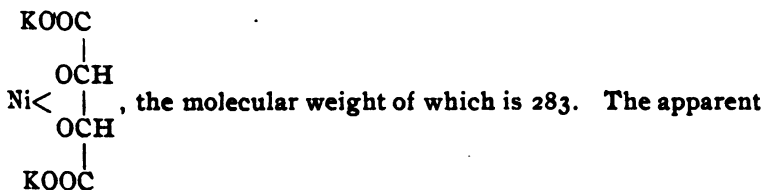
Referring to Table 5, it will be noticed that the depression gradually increases with the addition of potassium hydroxide from the fourth experiment to the seventh, except in No. 5. In this case the contents of the tube were viscous having the consistency of thin jelly, which interfered materially with the determination. This gelatinous mass completely dissolved on addition of more potassium hydroxide. The appearance of this substance is peculiar. The green liquid simply solidifies to a transparent mass without any change in appearance. On reversing the tube containing the substance it is found to be solid or viscous according to the amount of water present, and this is the only evidence of a change. On standing for a length of time it gradually becomes opaque. Several years ago this phenomenon was observed by Professor Bradley, of Middletown, who called my attention to it at that time. He obtained it by adding first tartaric acid to a solution of nickel sulphate and then adding a solution of potassium hydroxide drop by drop

¹ For the discussion of this, see Ostwald: *Ztschr. phys. Chem.*, 9, 553 (1892).

² See Table 5.

until the mass gelatinized. As can be seen from Table 5, it is formed when about one molecule of nickel tartrate is treated with one molecule of potassium hydroxide. It was shown just before the solution gelatinized (experiment 4, Table 5), that from the depression of the freezing-point and other considerations the molecule probably is $\text{KC}_4\text{H}_4\text{O}_8\text{NiONiO}_4\text{H}_2\text{C}_2\text{K}$. It is, therefore, possible that this gelatinous mass is a hydrated form of that substance. Heating almost to the boiling-point completely dissolves it.¹

To return to the effect on the depression of the freezing-point of adding potassium hydroxide, as seen in Table 5 from Experiment 4 on. Leaving out of consideration No. 5, where the solution was viscous, the increase in the depression from 0.134° to 0.156° and in the last case to 0.233° is by no means sufficient to be equal to the entire effect of the potassium hydroxide added, if it existed as such in the solution. 0.4935 gram more of potassium hydroxide was added in Experiment No. 7 than in No. 6. This quantity of potassium hydroxide should give normally a depression of 0.121° ,² but the difference between 0.233° and 0.156° is only 0.077° . In No. 7 the proportion of potassium hydroxide to nickel tartrate is two molecules of the former to one of the latter, or in the proper ratio to form



¹ Since writing this, Prof. Bradley has kindly allowed me to look over an unpublished manuscript by himself and F. A. Johnston on "A Tartrate of Sodium and Nickel," which treats of the formation, conduct, and gives some results of the analysis of this gelatinous substance. It was prepared from nickel sulphate, tartaric acid, and sodium hydroxide. It was isolated by stirring it up in alcohol, filtering and then washing with an equal volume of alcohol and water. When so treated the gelatine frequently remains transparent for a long time. It was found difficult to dry it to constant weight over sulphuric acid, for it is exceedingly hygroscopic. Preliminary analysis of the substance after drying over sulphuric acid showed: water, 7.04 per cent.; sodium, 6.30 per cent.; nickel, 21.04 per cent. We obtain by calculation from the above formula plus 2 molecules of water, $\text{Na}_2\text{Ni}_2\text{C}_4\text{H}_4\text{O}_{11} + 2\text{H}_2\text{O}$: water, 7.04 per cent.; sodium, 9.00 per cent.; nickel, 23.95 per cent. The most marked difference between these results and the results of the analysis is in the percentage of sodium. This may be accounted for from the fact that the gelatine is strongly alkaline and that washing removes some of this alkali, so that the residue may not have a constant composition. However, it is not asserted that the above formula represents the composition of the substance, for more analyses are needed in which the amount of tartaric acid is also determined, before the differences in the above results are explained and a suitable formula established.

² Calculated from the constant for potassium hydroxide reported by Raoult, *Ann. chim. phys.* (5), 28, 137 (1883).

molecular weight calculated from the depression, 0.233 is 185, which is a little more than half that calculated from the formula. Since such a substance would probably be dissociated in aqueous solution about as much as potassium tartrate,¹ it is very likely that a substance of the above formula does really exist in the solution. Nickel ions would not be expected to be present in any quantity in a solution of such a substance. The potential difference found between this solution and 0.1 mol. nickel nitrate is 0.256 volt (No. 6, Table 6). This shows that the concentration of the nickel ions is even less than in the preceding solution (No. 5), where the concentration of these ions was found to be $10^{-8.386}$. What has, therefore, probably taken place on the addition of potassium hydroxide from solution 4 to solution 7, Table 5, is that, although the potassium hydroxide is continually being removed from the field of action as such, the molecular structure of the substance in solution is undergoing a change; that is, the complex molecule, $\text{K}_2\text{C}_4\text{H}_4\text{O}_6\text{NiONiO}_4\text{H}_4\text{C}_4\text{K}$, is breaking up into the smaller molecule, $\text{K}_2\text{NiC}_4\text{H}_4\text{O}_6$; the number of molecules is, consequently, on the whole increased, and the depression of the freezing-point becomes greater.

TARTRATES OF COBALT.

Very little literature of a definite nature could be found on this subject. A tartrate of cobalt and a double tartrate of potassium and cobalt are mentioned in the following dictionaries of chemistry: Fehling's, Vol. 9 (1864); Watts', Vol. 5 (1868); Wurtz's, Vol. 3 (1878). Nearly all the early journals and such periodicals as Berzelius' *Jahresbericht*, Liebig and Kopp's *Jahresbericht*, the *Pharmaceutisches Centralblatt*, &c., were thoroughly searched, but no reference was found to the original articles describing these salts. Such works as Ladenburg's Dictionary, edition 1894, and Beilstein's, third edition, mention no such substances. It is, therefore, to be inferred that the original article contained nothing very definite. Fresenius² prepared certain racemates of cobalt, but gives no analyses.

Cobalt tartrate can be made in the same manner as nickel tartrate, by saturating hot tartaric acid with cobalt hydroxide

¹ See Kahlenberg, *loc. cit.*

² *Ann. Chem.* (Liebig), 41, 22 (1842).

or carbonate. It is thrown down as a pale pink powder practically insoluble in hot or cold water, and possessing in general the other properties of nickel tartrate. A sample of this dried at 120° gave 28.32 per cent. cobalt (theory, 28.49 per cent.).

When cobalt hydroxide is treated in the cold with tartaric acid it dissolves to a certain extent a pink solution resulting, which, on standing, deposits reddish pink crystalline scales of cobalt tartrate. This crystalline substance differs from the cobalt tartrate just described by being somewhat soluble in water. It is impossible to obtain as concentrated solutions of cobalt tartrate as of nickel tartrate, for the reason just mentioned, that some of the salt crystallizes out. With, however, as strong a solution as could be obtained the following determinations were made of the depression of the freezing-point.

TABLE 7.

Amount $\text{CoC}_4\text{H}_4\text{O}_6$ in 100 cc. solution. Gram.	Depression.	Apparent molecular weight.
0.6505	0.059 ⁰	207
0.3252	0.036	170
0.1626	0.021	146

Molecular weight of $\text{CoC}_4\text{H}_4\text{O}_6 = 207.1$.

These results run about the same as those obtained with solutions of nickel tartrate of similar concentration. The apparent molecular weight, 207, is very nearly equal to the molecular weight calculated from the formula; therefore, for the reasons already mentioned, the true molecular weight of cobalt tartrate is probably twice 207.1, which means its structure would be represented by twice the above formula or $(\text{CoC}_4\text{H}_4\text{O}_6)_2$. Table 8 gives the results of the determination of the electrical conductivity of solutions of this substance. The units are on the basis of equivalent ($\frac{1}{2} \text{CoC}_4\text{H}_4\text{O}_6$) in a liter as before.

TABLE 8.

m.	Temperature 18° .	L.
0.0628		15.9
0.0314		22.1
0.0157		28.7
0.0079		37.6
0.0039		47.1
0.0020		58.4
0.0010		69.9
0.0005		82.1

These results are entirely analogous to the conductivity of nickel tartrate (Table 2). They are abnormally small and show that cobalt tartrate is only slightly dissociated, which affords additional evidence that the molecule is polymerized.

Cream tartar acts vigorously on cobalt carbonate in the presence of water, the resulting solution being colored a deep pink. When this solution is evaporated over sulphuric acid, reddish pink crystalline scales are deposited, very similar in appearance to the deposit from a solution of cobalt tartrate. When almost to dryness the solution assumes a pasty nature, and can be completely dried only with considerable difficulty. No salt of the formula, $K_2CoC_2H_2O_{12}$, could be isolated. The crystalline deposit just mentioned yielded on drying 24.53 per cent. cobalt,¹ and a small quantity of potassium was also found. The deposit, therefore, consists largely of cobalt tartrate, but a small amount of potassium tartrate is mixed with it. Watts' "Dictionary," and the others above cited, say that potassium-cobaltous tartrate forms large rhomboidal prisms. No such crystals could be obtained by any of the methods used here. Determinations of the freezing-point of solutions prepared from cream tartar and cobalt carbonate yielded essentially the same results as similar solutions prepared from nickel carbonate. Such results might well be in harmony with the separate existence in the solution of potassium tartrate and cobalt tartrate, so no definite knowledge of the nature of the molecules in solution could be obtained by this method. Heating this solution causes the precipitation of a light pink powder. After washing this and drying at 120°, 28.38 per cent. cobalt was found which showed it to be cobalt tartrate. This substance possesses all the properties and is apparently identical with the cobalt tartrate previously mentioned.² It is to be noted that the conduct of this solution on heating is somewhat different from that prepared from nickel carbonate and cream tartar, for a flocculent precipitate resulted on heating this latter to boiling.

When potassium hydroxide is added to a solution of cobalt tartrate the conduct is very similar to that when it is added to a solution of nickel tartrate. It differs, however, in this respect,

¹ The theoretical percentage of cobalt according to formula $K_2CoC_2H_2O_{12}$, is 13.61.

² That prepared by treating hot tartaric acid with cobalt hydroxide.

that when the quantities of potassium hydroxide and cobalt tartrate are in the proportion of one molecule of the former to one of the latter, instead of obtaining a gelatinous mass, a *flocculent precipitate* results, which readily dissolves on further addition of potassium hydroxide. The range of the existence of this precipitate is considerable; that is, it begins to form when the amounts of the two substances are in about the ratio of one-half molecule of potassium hydroxide to one of cobalt tartrate, and does not entirely disappear until the potassium hydroxide is present in about the ratio of $1\frac{1}{2}$ molecules to 1 of the cobalt tartrate. This seriously interfered with following the effect on the freezing-point of successive additions of potassium hydroxide to cobalt tartrate. There is no difficulty, however, in determining the freezing-point of the solution when the potassium hydroxide is present in the ratio of two molecules of it to one of the tartrate; the results thus obtained are given in Table 9.

TABLE 9.

Amount $\text{CoC}_2\text{H}_3\text{O}_6$ in 100 cc. solution. Gram.	Amount KOH added. Gram.	Depression.
0.6505	0.0000	0.061°
0.6505	0.4530	0.106

If the molecular weight is calculated from the depression 0.106° , it gives 159, while according to the formula, $\text{K}_2\text{CoC}_2\text{H}_3\text{O}_6$, the molecular weight is 283.3. Owing to the dissociation which such a salt would suffer in aqueous solution, it is very probable that it exists here in the solution, and that it is due to its formation that cobalt hydroxide cannot be precipitated by alkalis from a solution of a cobalt salt to which tartaric acid has been added. The precipitate above referred to, formed when the amount of potassium hydroxide added to the cobalt tartrate is in the ratio of one molecule of the former to one of the latter, was filtered off and washed until the wash-water was no longer alkaline. It was then dried and the cobalt in it determined. In one sample the percentage of cobalt was 42.78 and in another 38.04. The precipitate has, therefore, no definite composition, but undoubtedly contains some cobalt hydroxide, for no conceivable tartrate of cobalt has as great a percentage of cobalt as was found.

SOLUBLE NICKEL SULPHIDE.

It is evident that when investigating the effect of an alkaline tartrate solution in preventing the precipitation of nickel sulphide by hydrogen sulphide, it is desirable to exclude the presence of other chemical substances. Tartaric acid and sodium hydroxide were, consequently; not added to a solution of a nickel salt, as for instance the chloride, for this would produce some sodium chloride, whose influence on the precipitation with hydrogen sulphide would then be entirely unknown. Solutions of pure nickel tartrate were prepared as has already been indicated, and to this the alkali and hydrogen sulphide were then added. If it was desired to note the effect of any neutral salt, as sodium chloride, on the precipitation, such salt was added separately. All the nickel tartrate used was made from nickel nitrate, which was a preparation of Schuchardt's and was marked "*purissimum*." According to Villiers,¹ sodium hydroxide is more effective in holding nickel sulphide in solution than potassium hydroxide. Solutions of nickel tartrate were treated with one equivalent of sodium hydroxide,² with two equivalents of sodium hydroxide, with three equivalents, and so on. Hydrogen sulphide was run into these solutions to saturation and the solutions filtered. In the first solution nickel sulphide was precipitated and the filtrate was only slightly colored, in the second the filtrate was a decided brown, in the third it was black, but to be certain that no nickel sulphide is precipitated it is necessary to have at least five equivalents of sodium hydroxide to one of nickel tartrate. This black filtrate oxidizes with remarkable rapidity, which is shown by the continual separation of sulphur. It is apparently the sodium sulphide present, which thus suffers oxidation, but what is peculiar, is that the oxidation is more rapid than ever takes place in a solution of sodium sulphide alone. The more dilute the solution, the less marked is the oxidation. If this black alkaline solution of nickel sulphide is allowed to stand for an indefinite length of time, the nickel sulphide gradually precipitates, so that in from five to ten days the supernatant liquid has usually become clear.

¹ Compt. rend., 119, 1263 (1894).

² By an equivalent of sodium hydroxide is meant that quantity which bears a ratio to the nickel tartrate used of 2 molecules NaOH to 1 molecule $\text{NiC}_4\text{H}_4\text{O}_6$.

This settling can be greatly accelerated by the presence of a neutral salt, as sodium chloride or potassium sulphate, the time necessary for settling varying with the amount of such salt added. The presence of a large quantity of these salts before the introduction of hydrogen sulphide causes a large portion of the nickel sulphide to be precipitated.

The behavior of this black solution of nickel sulphide seemed to indicate that it is not a true solution, but colloidal in nature. To decide this several tests were applied. With a high-power microscope it was impossible to detect solid particles of any sort. The following test employed by Muthmann¹ was applied: It consists in treating the solution in question with a solution of gum-arabic, shaking well, and then adding alcohol to precipitate the gum. If the substance is a colloid, it is precipitated with the gum and colors it. Before applying this test it is necessary to assure one's self that alcohol will not produce a precipitate in the original solution. In this case if the alcohol did not exceed 50 per cent. of the total liquid, nothing was precipitated, so care was exercised not to add more than this amount. The gum when precipitated was colored black, and on standing a few hours the supernatant liquid became clear. The alcohol was then poured off, and the residue treated with water, which dissolved it up again, the solution being colored black as before. This is the typical behavior of a colloidal substance. Tyndall's experiment applied by Picton² to solutions of antimony and arsenic sulphides was tried with this solution. The method employed was essentially this: The liquid in question was placed in a small bottle and the bottle so supported that the rays from an arc light could be focused directly on its bottom. The light, which diffused from the side of the bottle, was examined through a nicol. A colloidal solution of arsenic sulphide was first examined to see that the apparatus gave proper results. The light was polarized, which is in harmony with the results of Picton and the later ones of Stoekl and Vanino.³ The solution of nickel sulphide was then examined. On account of its dark color, it was necessary to use a very dilute solution so that the light would not be com-

¹ *Ber. d. chem. Ges.*, 20, 983 (1897).

² *J. Chem. Soc.*, 61, 143 (1892).

³ *Ztschr. phys. Chem.*, 30, 111 (1899).

pletely absorbed. With such a dilute solution no difficulty was experienced in getting it into the bottle, before the separation of any sulphur due to oxidation could take place. The light diffused from this solution was completely polarized. Some distilled water from which the solutions were made, was then placed in the bottle and examined in the same manner. No polarization could be detected. I am greatly indebted to Mr. H. W. Woodward of the physical department of this university for very efficient aid in these optical investigations. Independent observations by him in each one of the foregoing cases confirmed mine in every particular. All these tests, therefore, seem to show that nickel sulphide exists in an alkaline tartrate solution in the colloidal state; that is, as solid particles in an extremely finely divided condition, too small to be seen with any microscope but not so small but that they reflect light.

COBALT SULPHIDE.

Cobalt sulphide was produced in a manner exactly similar to that used in preparing soluble nickel sulphide. A solution of cobalt tartrate was made alkaline with a quantity of sodium hydroxide sufficient to hold nickel sulphide in solution, and then hydrogen sulphide run in to saturation. The cobalt tartrate was prepared from chemically pure cobalt chloride of Kahlbaum's, marked "*nickel frei*." After the hydrogen sulphide had been run into the alkaline solution, it was filtered. According to Villiers, the cobalt sulphide is entirely precipitated, but in nearly every case the filtrate was colored brown. Villiers points out that by this method one can detect the presence of nickel in most preparations of cobalt supposedly free from nickel. It was, therefore, expected that the brown coloration just referred to was due to the presence of a trace of nickel. This brown filtrate was refiltered two or three times, then shaken with sodium chloride, and allowed to stand over night. In the morning a slight black sediment had deposited and the supernatant liquid was perfectly clear. The deposit was filtered off, washed and dissolved in aqua regia. After removing the excess of acid, acetic acid and potassium nitrite were added, and the mixture left twenty-four hours, at the end of which time a well-defined

yellow precipitate had appeared. This shows conclusively that the brown color of the alkaline solution was due to cobalt sulphide in solution and not nickel, for not a trace of nickel could be found in the filtrate from the nitrite precipitate. This experiment was repeated several times and nearly every time some cobalt sulphide went into solution. The presence of a moderate quantity of a neutral salt, will, however, insure complete precipitation of the cobalt sulphide.

CONCLUSION.

The difficulties attendant on the separation of nickel and cobalt by the method of Villiers are the following: The oxidation of the solution to which the hydrogen sulphide has been added results in the separation of so much sulphur, that if nickel is present and cobalt is not, the black solution will color the sulphur, making it very difficult to distinguish from precipitated cobalt sulphide. Furthermore, according to the process used in this separation, sodium chloride is present in the solution, and although this aids in the complete precipitation of cobalt sulphide, it may cause some nickel sulphide to be precipitated, which in the absence of cobalt sulphide might readily be mistaken for it.

The nickel sulphide in solution in an alkaline tartrate medium is in the colloidal state.

Of the different tartrates of nickel and cobalt investigated, the most interesting are the solutions of the tartrates of these metals prepared from their hydroxides and cold tartaric acid. The results of determinations of the lowering of the freezing-point and of the electrical conductivity are very exceptional for salts of this sort, and seem to point to the existence of a polymerized molecular structure.

The evidence seems to be pretty conclusive, that the cause of the non-precipitation of the hydroxides of nickel and cobalt from solutions of their tartrates, or at least that any precipitate that may form dissolves in excess of the reagent, is due to the formation of a compound in which these metals replace the hydrogen atoms of the alcoholic hydroxyl groups of tartaric acid.

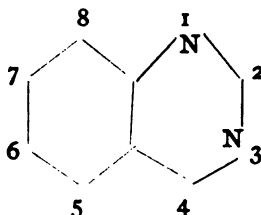
THE DIRECT SYNTHESIS OF KETODIHYDROQUINAZOLINS FROM ORTHOAMINO ACIDS.¹

BY MARSTON TAYLOR BOBERT AND AUGUST HENRY GOTTHELF.

Received June 26, 1900.

AS announced in our preliminary paper on this subject,² ketodihydroquinazolins (or oxyquinazolins) can readily be obtained by the action of nitriles upon orthoamino acids under conditions of heat and pressure. The present paper is confined to a discussion of the 2-methyl-4-ketodihydroquinazolin. Many others have been prepared and studied, and will form the subjects of later communications.

For convenience, throughout this article we have called our compound a "quinazolon" although we do not intend thereby to indicate any preference for the keto form as compared with the tautomeric oxyquinazolin form. The numbering for the quinazolin nucleus is that first suggested by Paal and Busch.³



Weddige⁴ the discoverer of this 2-methyl-4-ketodihydroquinazolin, obtained it from orthoacetaminobenzamide by fusion, by solution in alkalis with subsequent precipitation with acid, or by long boiling with water; also, by heating ethylorthoacetaminobenzoate to 160° C. with strong aqueous ammonia. Bischler and Burkart⁵ accomplished the same result by fusing the ammonium salt of orthoacetaminobenzoic acid, while Nientowski⁶ prepared it by heating together anthranilic acid and acetamide.

¹ Read before the joint meeting of the American Chemical Society and Section C of the American Association for the Advancement of Science, June 25, 1900.

² This Journal, 22, 129.

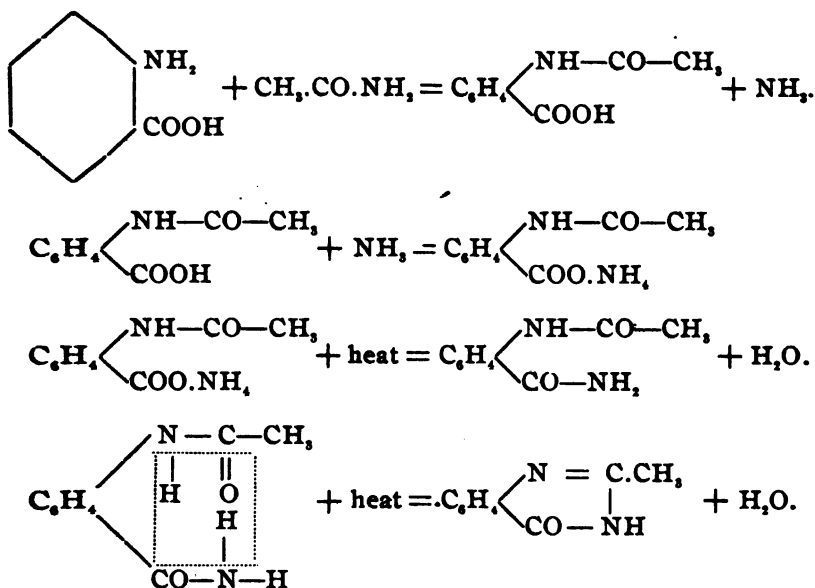
³ *Ber. d. chem. Ges.*, 22, 2684.

⁴ *J. prakt. Chem.* [2], 31, 124; 36, 143.

⁵ *Ber. d. chem. Ges.*, 26, 1350.

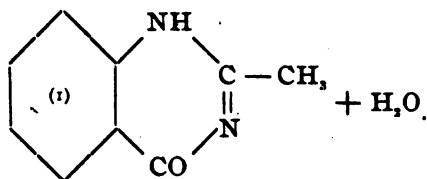
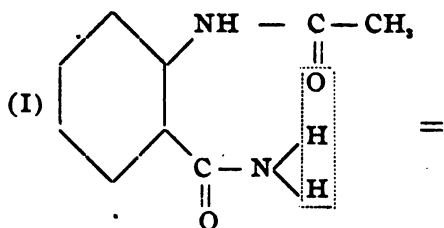
⁶ *J. prakt. Chem.* [2], 51, 364.

The syntheses of Weddige and Bischler are practically identical, both depending upon the formation of orthoacetaminobenzamide, from which the quinazolon results by loss of water. The course of Niementowski's synthesis is probably similar in the main, the following reactions being suggested in explanation:

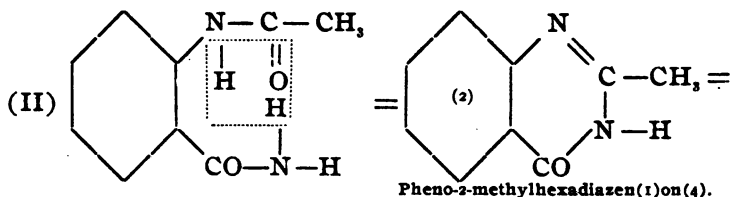


The first of these reactions seems probable when one remembers that acetanilide results from heating together aniline and acetamide, and that, with other amines, acetamide likewise yields the amide of the higher acid. The remaining reactions are then the same as in Bischler's synthesis.

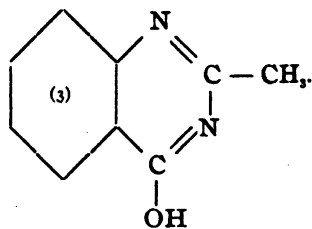
In all these syntheses there is an interesting point which should not be overlooked, and that is the manner in which the water splits out in the production of the quinazolon. By an examination of the formulas, it will be seen that this may occur in two different ways, one being a lactam condensation, the other equivalent to a lactim condensation, resulting in the production of two separate and distinct isomers, as follows:



Pheno-2-methylhexadiazen(2)on(4).

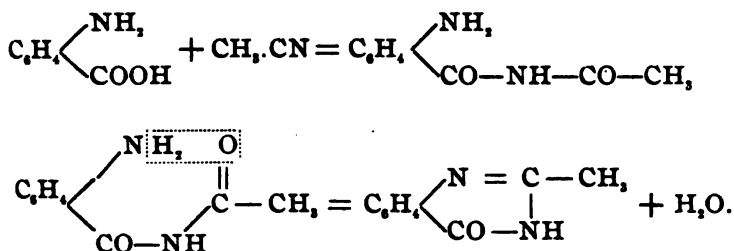


Pheno-2-methylhexadiazen(1)on(4).

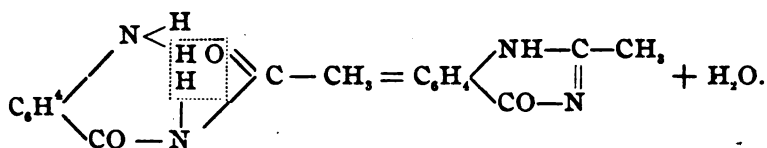
Pheno-2-methylhexadiazadien(1,3)on(4);
or 2-methyl-4-oxyquinazolin.

By a series of interesting reactions, Weddige proved his product to be (2) or (3), and the condensation, therefore, to have followed reaction (II). He did not, however, determine whether the compound appeared preferably in its keto or enol form, in his further studies of its properties. The products obtained by Bischler, by Niementowski, and by ourselves are identical in all respects with this compound of Weddige's, and the isomer represented by (1) is still unknown.

The conditions of our experiments resulting in the production of a quinazolon from anthranilic acid and nitriles were such that the first product of the reaction might be either a secondary amide, due to a condensation of the carboxyl and cyanogen groups or a transposition of groups might occur, giving anthranilic nitrile and acetic acid.¹ In the first case then, as our substance is identical with Weddige's, the reactions would be as follows :



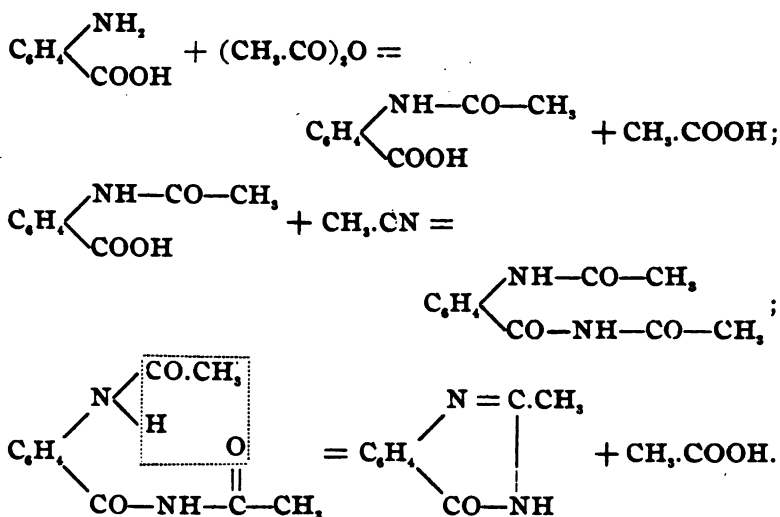
and not thus



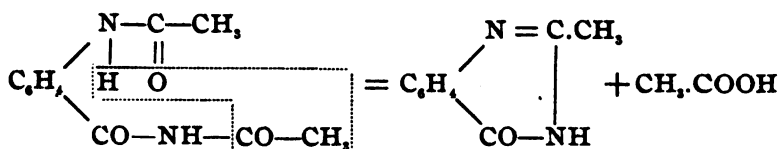
If this really represents the course of the reaction, it presents one or two interesting features. First, the elimination of water cannot here occur in the way described by Weddige, or an isomer would result with the double bond at (2) instead of at (1) as already mentioned. In regard to this point, however, it should be noted that this reaction is not exactly comparable with Weddige's, since in one case the condensation occurs with an aminic group, and in the other case with an amidic one. Another feature in which this synthesis differs from those already mentioned is in the position of the condensing acyl group, which here appears on the acid chain instead of in the amino group.

In later experiments, where acetic anhydride was present, the reactions would be similar :

¹ Compare Gautier: *Compt. rend.*, 67, 1255; and Colby and Dodge: *Am. Chem. J.*, 13, 1.

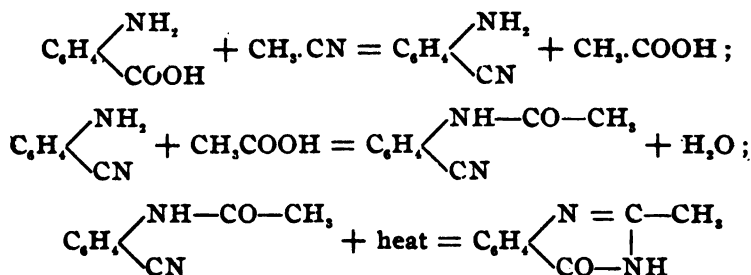


Although, in this case the possibility is not excluded of the reaction following the line indicated by Weddige :



In proof of the above reaction, acetylanthranilic acid was heated in a sealed tube with acetonitril, and the same quinazolón obtained.

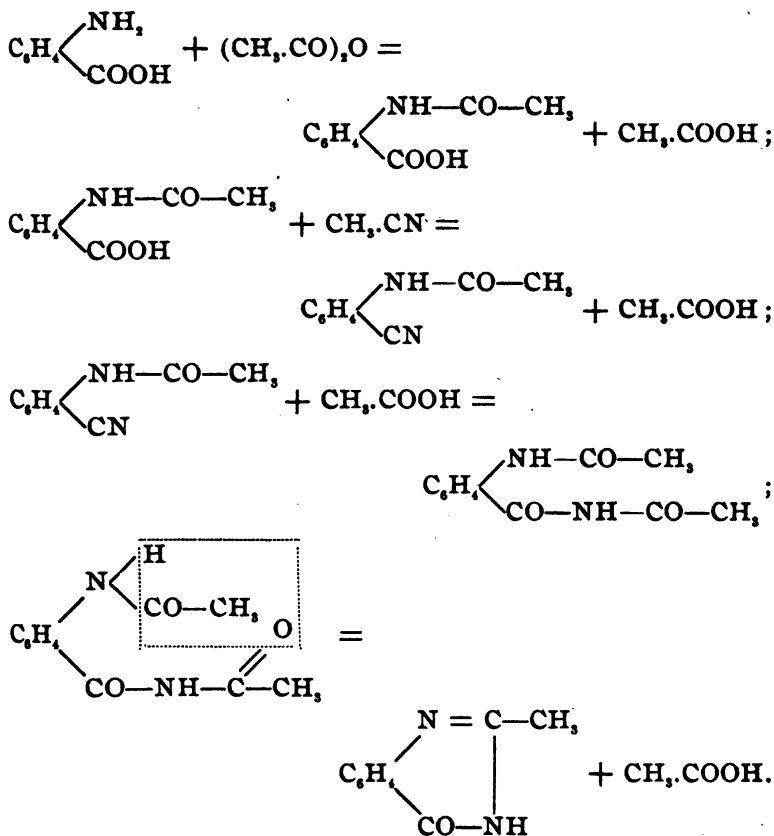
Another course which may be followed by the reaction is this:



The quinazolón being more stable at high temperatures than the anthranilic nitrile might cause such a rearrangement, but

Saemann,¹ who examined anthranilic nitrile, together with its acetyl and benzoyl derivatives, observed no such change. The production of anthranilic nitrile as the first phase of the reaction is more in accord with the results obtained by Colby and Dodge, but in some experiments carried out by us with the meta- and paraminobenzoic acids and acetonitrile we have been unable to isolate any aminobenzonitriles, although similar experiments with the three nitrobenzoic acids readily yielded the corresponding nitrobenzonitriles.

In our first experiments equal molecules of acid and nitrile were used, but in all of the later ones acetic anhydride was also added, and the reaction will then be slightly different :



¹ Ber. d. chem. Ges., 29, 631.

We, therefore, prepared some acetylanthranilic nitrile and heated it with acetic anhydride in a sealed tube, the result being the same quinazolon as before. Such a reaction is not likely to have taken place in the tubes where no acetic anhydride was used, for there would have been no excess of acetic acid to combine with the nitrile for the production of the secondary amid, the acetic acid reacting first, of course, with the amino group.

To sum up then, it seems most probable to us that the course of the reactions is as follows:

1. *In Absence of Acetic Anhydride.*—Condensation of the carboxyl and cyanogen groups to a secondary amide, which passes into the quinazolon by loss of water.

2. *In Presence of Acetic Anhydride.*—Production of acetylanthranilic acid, with subsequent combination of carboxyl and cyanogen groups, the resulting secondary amide yielding the quinazolon by loss of acetic acid.

EXPERIMENTAL PART.

Synthesis of 2-methyl-4-ketodihydroquinazolin from anthranilic acid and acetonitrile.

Anthranilic Acid and Acetonitrile.—One molecule of anthranilic acid and 2 or 3 molecules of acetonitrile were heated together in a sealed tube for six hours at 200°–210° C. The tube then contained a crystalline mass wet with a dark liquid, and when opened evolved carbon dioxide with considerable force. The mass was extracted with ether, and the ether solution filtered. On driving off the ether from the filtrate a brown oil remained together with a small amount of a crystalline substance. This oil was driven over with steam and found to be aniline, while the crystalline substance was identified as acetanilide. The carbon dioxide and aniline were the usual decomposition products of the anthranilic acid, the acetanilide being formed by a secondary reaction between aniline and acetic acid or aniline and acetamide.

The residue insoluble in ether consisted of needles which, recrystallized from water and bone-blackened, melted at 232°–233° C. (238°–239° C. corr.). These crystals were insoluble in cold water, soluble in hot, and partly soluble in hot chloroform. The

aqueous solution was acid to litmus, but did not decompose sodium carbonate solution, or dissolve freshly precipitated silver oxide when boiled with it. They readily dissolved in concentrated potassium hydroxide solution, but underwent no decomposition when the solution was boiled; but when this same alkaline solution was boiled with excess of concentrated hydrochloric acid and then cooled, long transparent needles of a hydrochloric acid salt were obtained, which sublimed before melting and gave the free base again (m. p. 232° C.) when treated with sodium carbonate solution. An aqueous solution of the free base gave the following reactions: with copper sulphate solution, a light blue precipitate; with silver nitrate solution, a white precipitate; with stannous chloride solution, a gelatinous precipitate, dissolving on heating and separating out in needles on cooling; with cobalt nitrate solution, a voluminous curdy precipitate, blue in presence of any excess of alkali; with mercuric chloride solution, a curdy white precipitate; with lead acetate solution, a curdy white precipitate. An aqueous solution of the hydrochloric acid salt gave a dark yellow precipitate with neutral potassium chromate, and an orange-red one with platinum chloride.

The free base crystallizes from water in transparent prisms or needles, carrying 1 molecule of water of crystallization which they readily lose at 100° C. An analysis of the crystals, dried at 100° C. gave the following results:

I. 0.1582 gram substance gave 0.3904 gram carbon dioxide, and 0.0711 gram water.

II. 0.1584 gram substance gave 0.3898 gram carbon dioxide, and 0.0722 gram water.

III. 0.1466 gram substance gave 0.3628 gram carbon dioxide, and 0.0666 gram water.

IV. 0.1613 gram substance gave 26 cc. nitrogen at 24° C. and 756 mm.

V. 0.1468 gram substance gave 23.8 cc. nitrogen at 22.5° C. and 750 mm.

	Calculated for $C_9H_8N_2O$.	I.	II.	Found. III.	IV.	V.
Carbon.....	67.50	67.30	67.11	67.49
Hydrogen.....	5.00	4.99	5.06	5.04
Nitrogen.....	17.50	17.97	18.07
Oxygen.....	10.00
	<hr/> 100.00					

The molecular weight was also determined by the freezing-point method, using glacial acetic acid as the solvent:

Weight of substance taken.....	0.3184 gram.
" " glacial acetic acid.....	23.7600 grams.
Freezing-point of acetic acid.....	4.05°
" " " mixture.....	3.71°
Lowering of freezing-point.....	0.34°
K.....	3880.0
Molecular weight	153.0
" " of $C_9H_8N_2O$	160.0

The substance is hence identical with the 2-methyl-4-ketodihydroquinazolin of Weddige, Bischler, and Niementowski.

One of the first difficulties encountered in this synthesis is the tendency of the anthranilic acid to break up into carbon dioxide and aniline, and we have not been able as yet to overcome this entirely. Very gradual heating of the tube contents, even when long continued, did not appear to give any better yield than direct heating at 200°–210° C. for six or eight hours. The water split off in the reaction was also found to exert a most harmful influence upon the products, causing decomposition and the formation of much tar. The use of an excess of acetonitrile improved the yield somewhat, and the addition of acetic anhydride was found particularly beneficial in this respect. By using nearly enough anhydride to take up all the water split off, the yield was nearly doubled, being brought up to 45 per cent. of the theory, while the tube contents were invariably light colored and free from tar.

Syntheses of Bischler and Burkart, and of Niementowski.—For purposes of comparison some 2-methyl-4-ketodihydroquinazolin was prepared by the method of Bischler and Burkart, and of Niementowski.

Bischler and Burkart's Synthesis.—Acetylanthranilic acid was neutralized with ammonia, the solution evaporated to crystals, and the product recrystallized. Fusion of these crystals for twenty minutes gave a yield of the quinazolone amounting to about 25 per cent. of the weight of the acetylanthranilic acid used. Dehoff,¹ who was the first to suggest this method, abandoned it as unsatisfactory, but his difficulty seems to have been in getting a pure anthranilic acid to start with.

¹ *J. prakt. Chem.* [2], 42, 347.

Niementowski's Synthesis.—This investigator states that by fusing together acetamide and anthranilic acid for six to eight hours at 135°–155° C. a yield of quinazolon may be obtained equal to half the weight of the anthranilic acid used. Our experience indicated that twenty-four hours' heating at this temperature was necessary to remove all ammonia, and the yield of quinazolon was only about half that given by Niementowski. By treating the melt with ether the quinazolon remains insoluble and can thus be separated and recrystallized. In the ethereal washings we have isolated, in addition to acetanilide, a substance crystallizing from water in flat needles with jagged edges, and melting at 190°–191° C. (194°–195° C. corr.). This melting-point could not be altered by repeated crystallizations, from water, and the substance cannot therefore be impure quinazolon. With metallic potassium or sodium the presence of nitrogen in this substance is easily demonstrated, but boiling with concentrated potassium hydroxide solution produces no ammonia, aniline, or other primary amine, for no isonitrile odor could be detected after the addition of chloroform, and it does not seem possible, therefore, that the compound can be amidic in character. That it probably represents an intermediate step in the reaction, however, is clearly shown by the fact that it can be converted to the quinazolon by boiling with concentrated hydrochloric acid or by sublimation. We are now endeavoring to prepare sufficient of this material to determine its structure, in the hope that it may throw considerable light upon the course of this interesting synthesis.

PREPARATION OF DERIVATIVES OF 2-METHYL-4-KETODIHYDRO-QUINAZOLIN.

Three sets of derivatives were prepared for purposes of comparison, one from quinazolon obtained by Bischler's synthesis, another from quinazolon obtained by Niementowski's synthesis, and a third set from our own product. An examination of similar derivatives in the three sets showed them in every case to be identical in all points irrespective of the source of the quinazolon.

Hydrochloride.—Prepared by boiling the free base, or its alkaline salts, with excess of concentrated hydrochloric acid. As the solution cools the hydrochloride crystallizes out in long trans-

parent needles, often of a decided yellowish cast and with a strong greenish fluorescence. These needles sublime without decomposition or dissociation, and do not break up at 336° C. as reported by Niementowski.¹

Chlorplatinate.—By the addition of platinic chloride to a hot solution of the hydrochloride the chlorplatinate gradually separates on cooling in coarse red crystals, which can be recrystallized from water. Frequently unchanged hydrochloride will persistently separate with the chlorplatinate even after prolonged boiling with excess of platinum chloride.

	Calculated for (C ₉ H ₈ N ₂ O.HCl) ₂ PtCl ₄ .	I. Found.	II.
Pt	26.61	26.62	26.78

Nitrate.—When the free base is boiled with an excess of nitric acid (1 : 4), and the solution allowed to cool, the nitrate separates in white needles, which decompose at about 185° C. Niementowski found his product to decompose at 195° C.

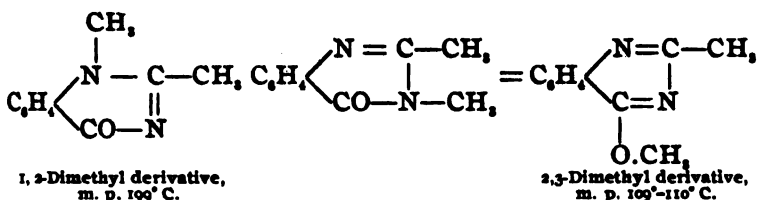
Chromate.—This salt was prepared both by the addition of potassium chromate to a solution of the hydrochloride, and also by heating the free base with chromic anhydride. It forms yellow crystals, beginning to blacken at 176° C. rather than at 182° C. as reported by Niementowski.

	Calculated for C ₉ H ₈ N ₂ O.CrO ₃ .	Found.
Cr	20.00	19.41

Methyl Ether.—Equal molecules of 2-methyl-4-ketodihydroquinazolin, potassium hydroxide, and methyl iodide are dissolved in alcohol, and the mixture heated several hours on the water-bath with a return condenser. The alcohol is driven off, and the residue crystallized from water. It then forms white needles, melting at 71° C. (72° C. corr.) in the hydrated condition, and at 109°–110° C. (110°–111° C. corr.) when anhydrous, thus identifying it with the β,γ -dimethyl- Δ -pseudoxyquinazoline of Weddige,² and proving conclusively the structure of the original 2-methyl-4-ketodihydroquinazolin, for the isomeric pheno-2-methylhexadiazon(2)on(4) yields a dimethyl derivative melting at 199° C. The structure of these isomeric dimethyl derivatives is as follows :

¹ Ber. d. chem. Ges., 29, 1360.

² J. prakt. Chem. [2], 38, 151.



It seems most likely, in view of recent work upon similar compounds, that the 2-methyl-4-ketodihydroquinazolin reacts with alkalis in its pseudo or enolic form, and that the dimethyl derivative mentioned above contains the second methyl group attached to oxygen and not to nitrogen, thus giving an ether of a true methyl quinazolin. This would also explain why the 2,3-dimethyl derivative has a melting-point so much lower than its isomer, for in the 2-methyl-4-ketodihydroquinazolin compound with the double bond at (2) the carbonyl is para to the imido group, and it could not therefore so easily pass into a pseudo-enolic form.

SYNTHESIS OF 2-METHYL-4-KETODIHYDROQUINAZOLIN FROM ACETYLANTHRANILIC ACID.

Acetylthranilic Acid.—This was prepared by the method of Jackson,¹ from anthranilic acid and acetic anhydride. Anthranilic acid was boiled for three hours with twice the theoretical amount of acetic anhydride. On cooling nothing separated, so the mixture was precipitated by pouring into water, the mass then warmed slightly to decompose any excess of anhydride, and the precipitate filtered out and washed. This precipitate was next dissolved in ammonia water, reprecipitated by hydrochloric acid, the precipitate filtered out and crystallized from water, when it formed plates melting at 182° – 184° C. Occasionally it separated in a gelatinous mass on crystallization, showing a slightly lower melting-point (181° – 183° C.), due possibly to difficulty in getting it perfectly dry.

In all cases, a small amount of the precipitate obtained by the addition of hydrochloric acid to the ammoniacal solution refused to dissolve in boiling water. This insoluble portion was separated and crystallized from glacial acetic acid, yielding fine white needles, melting at 221° – 223° C. This is probably the diacetyl

¹ *Ber. d. chem. Ges.*, 14, 886.

derivative, but not enough was obtained for further investigation. Jackson,¹ reports similar results in his preparation of the acetylanthranilic acid.

Diacetylanthranilic Acid.—Bedson² states that when acetic anhydride and anthranilic acid are boiled together for some time under a return condenser the mixture solidifies on cooling to a crystalline mass of diacetylanthranilic acid. We have been unable to confirm this, as was the case apparently with Jackson also.

Anthranilic acid was boiled for several hours with acetic anhydride under a return condenser, but nothing separated on cooling. On addition of water a precipitate was obtained which, on recrystallization, proved to be impure monacetylanthranilic acid, melting at 175°–185° C. Another portion of anthranilic acid was heated with acetic anhydride until all excess of anhydride had been driven off. The residue was then dissolved in alcohol, the solution bone-blackened and evaporated, leaving a tarry mass from which hot benzene extracted a substance melting at 178°–182° C. on recrystallization, and which was evidently only impure monacetylanthranilic acid. Monacetylanthranilic acid was then boiled for ten hours with acetic anhydride, decomposition apparently setting in at this point, for when the mass was poured into water it produced a yellow milky solution with much tar.

The effect of pressure was next tried. Five grams of anthranilic acid, 9 cc. of acetic anhydride, and 10 cc. glacial acetic acid, were heated together in a sealed tube for five hours at 160°–170° C. The contents of the tube then appeared liquid, and no pressure was detected on opening the tube. The excess of acetic acid and anhydride was removed by distillation, and the residue left in a desiccator over potassium hydroxide, where it gradually solidified to a crystalline mass, some of which recrystallized from benzene melted at 180°–182° C. and proved to be the monacetyl derivative again. We have, therefore, failed to get any appreciable amount of diacetylanthranilic acid by the methods employed.

Acetylanthranilic Acid and Acetonitrile.—Five grams of acetylanthranilic acid and 7 cc. acetonitrile were heated together in a sealed tube for four and a half hours at 220°–210° C. The tube

¹ *Loc. cit.*

² *J. Chem. Soc.*, 37, 756.

was then filled with needle crystals and a dark brown liquid. No pressure was evident upon opening the tube. The liquid was decanted carefully from the crystals and the latter washed with dilute sodium carbonate solution, to remove unchanged acid, etc. The residual crystals dissolved in alcohol, bone-blackened, and the solution evaporated, yielded coarse needles melting at 232° – 236° C. and readily identified with the 2-methyl-4-ketodihydroquinazolin prepared by the methods already mentioned.

To prove that no acetyl derivative of the quinazolon was produced in this reaction, 0.5 gram of the quinazolon was boiled for one hour with 5 cc. acetic anhydride, and on cooling long needles separated exactly similar to those obtained from the above reaction. That these were really only the original quinazolon was shown by the molecular weight determination, by the freezing-point method, with glacial acid as the solvent:

Weight of substance	0.4637 gram.
" " acetic acid	23.3805 grams.
Freezing-point of acetic acid	4.04°
" " mixture	3.57°
Lowering of freezing-point	0.47°
K	3880.0
Molecular weight	163.7
" " of $C_9H_8N_2O$	160.0
" " $C_9H_7N_2O(CO.CH_3)$	202.0

Acetyl chloride was found to have no action upon the quinazolon under ordinary conditions.

The experiments with anthranilic nitrile, acetylanthranilic nitrile, and similar orthoaminonitriles, form the subject of another paper.

In conclusion, then, the following new syntheses of 2-methyl-4-ketodihydroquinazolin have been discovered:

1. By heating orthoamino acids, or their acyl derivatives, with nitriles.
2. By heating orthoaminonitriles, or their acyl derivatives, with acids.

The extension of these syntheses to other acids and nitriles is now under way. We are also studying the action of nitriles upon α - and β -amino acids and their nitriles both aliphatic and aromatic, as well as the action of nitriles upon other classes of orthosubstituted acids.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 27.]

NOTES ON LEAD AND CADMIUM FERROCYANIDES.

BY EDMUND H. MILLER AND HENRY FISHER.

Received June 29, 1900.

LEAD FERROCYANIDE.

THE following series of experiments were made in order to ascertain whether the composition of lead ferrocyanide is invariably $\text{Pb}_2\text{Fe}(\text{CN})_6$, or whether, like the ferrocyanides of manganese and zinc, it is affected by the conditions of precipitation.

The precipitates were made as follows: Lead acetate was dissolved in water and heated to boiling, to this a hot aqueous solution of potassium ferrocyanide was added, and acid in some cases as is noted later. The precipitates were allowed to settle and were washed by decantation until free from lead or ferrocyanide as indicated by hydrogen sulphide, or by ferric chloride. They were then dried at 105°C. to constant weight. The method of analysis was in all cases as follows: About one gram was dissolved in dilute nitric acid in a casserole, and after the addition of sulphuric acid, evaporated to fumes. One evaporation was found to effect complete decomposition. The residue was taken

up with 1 per cent. sulphuric acid to which half its volume of alcohol was added. The lead sulphate was washed with 1 per cent. sulphuric acid containing alcohol, filtered and weighed in a Gooch crucible. The iron was precipitated in the filtrate by ammonia, after boiling out the alcohol and adding ammonium chloride, filtered, washed, and weighed as Fe_2O_3 . The filtrate from the iron was evaporated to dryness in platinum, the ammonia salts volatilized and the potassium sulphate weighed.

A. Precipitate formed in a neutral solution with lead in excess, settles rapidly. The analytical results are :

	I.	II.	III.	Average.
Lead	66.03	66.15	66.09	66.09
$\text{Fe}(\text{CN})_6$	34.07	33.98	33.85	33.97
Potassium	0.50	0.48	0.45	0.47
				100.53

B. Solution neutral, ferrocyanide in excess, the precipitate settles slowly. It gave on analysis :

	I.	II.	III.	Average.
Lead	66.26	66.06	65.98	66.10
$\text{Fe}(\text{CN})_6$	33.54	33.77	33.90	33.70
Potassium	0.62	0.55	0.58	0.58
				100.38

C. Solution slightly acid with acetic acid, lead in excess. The precipitate settles rapidly. On analysis the following results were obtained :

	I.	II.	III.	Average.
Lead	64.42	64.55	64.62	64.53
$\text{Fe}(\text{CN})_6$	35.48	35.33	35.37	35.39
Potassium	0.84	0.81	0.80	0.82
				100.74

D. Solution slightly acid with acetic acid, ferrocyanide in excess. Precipitate settles rapidly. The results on analysis were almost identical with those obtained from the preceding precipitate.

	I.	II.	III.	IV.	Average.
Lead	64.43	64.28	64.38	64.58	64.42
$\text{Fe}(\text{CN})_6$	35.47	35.62	35.69	35.60	35.59
Potassium	0.82	0.76	0.86	0.79	0.81
					100.82

E. Solution strongly acid with acetic acid, ferrocyanide in excess. Precipitate settles badly. The results are:

	I.	II.	Average.
Lead.....	63.73	64.02	63.87
Fe(CN) ₆	35.51	35.02	35.26
Potassium.....	0.76	0.96	0.86

These and the following are results calculated from the determination of potassium, lead, and iron in undried portions and consequently, when calculated from the ratio of Fe : K : Pb, add up to 100 per cent.

F. Solution strongly acid with hydrochloric acid, ferrocyanide in excess, precipitated hot as usual.

	I.	II.	Average.
Lead.....	63.02	63.39	63.21
Fe(CN) ₆	34.74	34.48	34.61
Potassium.....	2.24	2.12	2.18

When the analysis is made on a sample dried to constant weight, it invariably adds up to a little over 100 per cent. This is probably caused by the fact that on drying, the precipitates become either bluish or greenish in color due to a slight decomposition so that the percentages of Fe(CN)₆, which are calculated from the iron are high.¹

It is evident from these results that the precipitate varies in composition under different conditions of precipitation, and as the acidity increases the percentage of potassium increases and that of lead diminishes.

Also, that when the acidity is the same the composition is the same whether ferrocyanide or lead is in excess.

Berzelius² states that when formed in a neutral solution with potassium ferrocyanide in excess, the composition of the precipitate is Pb₂Fe(CN)₆. Using the most recent atomic weights this corresponds to a percentage composition of:

Lead	66.10
Fe(CN) ₆	33.90

Our results are, with lead in excess:

Lead	66.09
Fe(CN) ₆	33.97

¹ For the CN : Fe ratio is higher in Fe(CN)₆ than in Fe₂(CN)₁₀ or Fe₃(CN)₁₅.

² *Ann. Chem. Phys.*, 15, 157 (1820).

With ferrocyanide in excess :

Lead	66.10
$\text{Fe}(\text{CN})_6$	33.70

The only statement we have found suggesting any variation in the composition of this ferrocyanide is by Gay-Lussac¹ that "the precipitate for however long a time it may have been washed, retains from 6-9 per cent. of ferrocyanide of potassium; of which it continues to give up a certain quantity to fresh portions of water." The conditions of this precipitation are not stated.

In order to compare these results with those obtained by titration, the following experiments were made. A solution of potassium ferrocyanide was very carefully standardized against metallic zinc and freshly ignited zinc oxide. The conditions being; bulk 200 cc., acidity 2 cc. concentrated hydrochloric acid, temperature about 80° C. Uranium acetate was used as an indicator on porcelain. An allowance of 0.3 cc. was made in each case for the excess necessary to affect the indicator. The results of six concordant determinations gave as the strength of this solution, 1 cc. = 0.005857 gram of zinc.

This solution was then used to titrate solutions containing known weights of lead as follows :

Neutral Solution.—Separate portions of metallic lead, of about 1 gram each, were dissolved in nitric acid, hydrochloric acid added and evaporated to complete dryness; the lead chloride was then dissolved in hot water diluted to 200 cc. and titrated. The titration in a neutral solution is not altogether satisfactory. Five determinations gave results varying from 0.02454 to 0.02461. Average, 0.02458.

Acetic Acid Solution.—Six determinations gave from 0.02450 to 0.02458; the average coinciding with the two most satisfactory titrations is 0.02454 gram.

Hydrochloric Acid Solution.—In a solution containing one drop of concentrated hydrochloric acid the results were from 0.02441 to 0.02446; average, 0.02444 gram. With 1 cc. of hydrochloric acid the results were unreliable on account of the solubility of the precipitate.

¹ Gmelin's "Handbook of Chemistry" (London, 1852), Vol. VII, p. 490.

Assuming that the precipitates formed are in one case $Zn_3K_2(Fe(CN)_6)_2$, and in the other $Pb_3Fe(CN)_6$, or that an amount of ferrocyanide which precipitates three atoms of zinc precipitates four of lead, the factor by which the zinc standard must be multiplied to give the lead standard is 4.218. This gives by calculation from the zinc standard, 0.0247 as the lead standard of the solution.

The amounts of lead precipitated per cubic centimeter in no case reach this value and although the variations are not so great as is shown from the analyses of the precipitates, they are in exactly the same order, and so confirm the statement that increase of acidity tends to diminish the percentage of lead in the precipitate.

Our results agree closely with Low's¹ statement: that a solution containing 10 grams per liter of crystallized potassium ferrocyanide will equal 10 milligrams of lead per cubic centimeter, and are at complete variance with a statement by Furman² that it requires 16 grams per liter for such a solution. Furman's figure is evidently based on the assumption that this value can be determined by a direct ratio between lead and zinc.

CADMIUM FERROCYANIDE.

The potassium ferrocyanide solution, already described, was used to titrate a number of solutions containing cadmium under different conditions. Portions of cadmium oxide of 0.3 to 0.4 gram each were dissolved in hydrochloric acid, and evaporated to complete dryness, then dissolved in 200 cc. of hot water and titrated. It was found that uranium acetate on porcelain was very unsatisfactory as the precipitate reacts with the indicator as is the case with manganese, so that the end tests in these titrations were made on filter-paper placing the drops so that the precipitate of cadmium ferrocyanide did not come in contact with the uranium acetate.

The results in a neutral solution were not concordant, varying between 0.0071 and 0.00727 gram of cadmium per cubic centimeter.

In a solution containing 1 cc. of 50 per cent. acetic acid the

¹ This Journal, 15, 550 (1893).

² "Manual of Practical Assaying," p. 139.

results ran from 0.00699 to 0.00702 gram of cadmium; average, 0.0070 gram.

In a solution containing 1 to 2 cc. of concentrated hydrochloric acid the average of six determinations on cadmium oxide gave 1 cc. = 0.007177 gram of cadmium; this was checked by four tests with metallic cadmium which gave 0.007165 gram, or a general average of 0.00717 gram. Another set was made with only a few drops of hydrochloric acid present; these gave almost the same results. With this solution it was found possible to use uranium acetate on porcelain but drops on filter-paper are a safer end-point for cadmium titrations.

As cadmium hydroxide is soluble in ammonia it was possible to extend the titration to an ammoniacal solution by using as an indicator a 4 per cent. solution of copper sulphate, as recommended by Moldenhauer¹ for zinc. The spots are made on filter-paper, as already described; the end-point, a red line, is distinct but not as delicate as with uranium acetate. An allowance of 0.9 cc. was made for the excess necessary to affect the indicator. Four tests gave the following values for 1 cc.: 0.00669, 0.00678, 0.00674, 0.00674; average, 0.00674 gram of cadmium per cubic centimeter.

The formula usually assigned to cadmium ferrocyanide is that given by Hermann:² $\text{CdK}_2\text{Fe}(\text{CN})_6$; assuming that this is the composition of the precipitate, the ratio as regards ferrocyanide is $3\text{Zn} = 2\text{Cd}$, and the strength of the ferrocyanide solution used would be 1 cc. = 0.00671 gram cadmium. The results of the titrations do not agree with this value except those obtained in an ammoniacal solution.

Other formulas have been given for cadmium ferrocyanide. Dammer gives it the normal composition $\text{Cd}_2\text{Fe}(\text{CN})_6$ and cites Wittstein³ as his authority, but the original article gives neither formula nor analysis.

Wyruboff⁴ gives the composition under all conditions as $\text{K}_2\text{Cd}_2(\text{Fe}(\text{CN})_6)_2$, which has been altered in Comey's "Dictionary," so as to satisfy the valence of the $\text{Fe}(\text{CN})_6$ radical to $\text{K}_2\text{Cd}_2(\text{Fe}(\text{CN})_6)_2$. Assuming that this is the precipitate formed, the

¹ *Chem. Ztg.*, 13, 1220 (1889), and 15, 223 (1891).

² *Ann. Chem. u. Pharm.*, 145, 235 (1868).

³ *Büchner's Repertorium der Pharm.*, 63, 316-317.

⁴ *Ann. chim. phys.* [5], 8, 449 (1878).

ratio as regards ferrocyanide becomes $6\text{Zn} = 5\text{Cd}$, and the strength of the solution used would be 1 cc. = 0.00838 gram cadmium.

Our results in acid solutions are intermediate between these values and indicate a variation in the composition of the precipitate between the formulas of Hermann and of Wyrupboff. They are confirmed by a statement by Mackay¹ that it requires about $2\frac{1}{2}$ per cent. less potassium ferrocyanide to precipitate cadmium than is required by the formula $\text{CdK}_4\text{Fe}(\text{CN})_6$, or in other words the cadmium standard is higher than would be obtained by calculation. They are again in direct contradiction to the statement by Furman that the cadmium standard can be obtained from the zinc standard by direct proportion assuming that $2\text{Zn} = 2\text{Cd}$.

In order to ascertain the composition of cadmium ferrocyanide under different conditions analyses of the precipitates must, of course, be made. This work has already been started and while no results have yet been obtained the marked difference in the physical properties of the precipitates seems to confirm the variation in composition.

COLUMBIA UNIVERSITY,
June 27, 1900.

[CONTRIBUTION FROM THE LABORATORY OF THE NORTH CAROLINA
AGRICULTURAL EXPERIMENT STATION.]

THE DIGESTIBILITY OF SOME NON-NITROGENOUS CON- STITUENTS OF CERTAIN FEEDING-STUFFS.²

By G. S. FRAPS.

Received June 16, 1900.

THE ether extract, protein, nitrogen-free extract, and crude fiber, which are determined in ordinary feeding-stuff analyses, are groups of compounds, and are composed of various substances with different properties and different coefficients of digestibility. The ether extract may contain (besides the true fats) waxes, cholesterin, phytosterin, lecithin, hydrocarbons, coloring-matters, etc. "Protein" includes amido compounds, acid amides, organic bases, ammonia, and nitrates, besides products of varied nature, one of which, nuclein, is entirely indiges-

¹ This Journal, 21, 940 (1899).

² This work was suggested to the author by Prof. W. A. Withers, Chemist of the Station. See Bulletin 172.

tible. The nitrogen-free extract may contain sugars, dextrin, gums, starches, pentosans, coloring-matters, organic acids, lignocellulose and cellulose, the two latter remaining in part in the crude fiber. The crude fiber contains cellulose, lignocellulose, etc. Considering the number of substances which may enter into the composition of the fodder-groups, and the variations which take place in the quantity present, it is not surprising that the digestibility of these groups differs greatly with different feeding-stuffs.

The digestibility of some of the proximate constituents of feeding-stuffs has been determined, or, more correctly, groups of proximate constituents, namely, the sugar group, the starch group, and the pentosan group. All three of these groups have not been determined on the same material. The work about to be described in this paper has given a basis for calculating the digestibility of certain proximate groups, which can be arranged in the following tentative order, according to their digestibility: Sugars, starches, pentosans, crude fiber, residual nitrogen-free extract, and pentosans in the crude fiber. The number of digestion experiments made is not large, but it is not believed that future experiments will materially modify the order above given. This Station expects to continue the work along this line.

The materials used in this work are from digestion experiments on sheep, one described in Bulletin 148 of this Station, six described in Bulletin 160, one not yet published. Excepting timothy hay No. 1, all figures are means of experiments with two sheep.

DIGESTIBILITY OF SUGARS.

W. H. Jordan, J. M. Bartlett, and L. H. Merrill, at the Maine Experiment Station,¹ found that the sucrose and reducing sugars in alsike clover, white clover, blue joint, orchard grass, red top, timothy, wild oat grass, witch grass, buttercup, and white weed were completely digested. E. F. Ladd, at the New York (Geneva) Experiment Station,² found the sucrose and reducing sugars to be completely digested in alfalfa hay, mixed hay, wheat bran, corn-meal, cottonseed-meal, linseed-meal, and oats; the

¹ Report 1888, 98.

² Report 1889, 149.

sucrose in turnips fed with mixed hay was digested only 78.7 per cent., the reducing sugars being completely digested. B. W. Kilgore and F. E. Emery, at the North Carolina Station,¹ found the reducing sugars completely digested in corn-fodder, crimson clover hay, cowpea vine hay, soja-bean silage, cottonseed, and cottonseed hulls. H. C. Sherman² found the glucose and sucrose (soluble carbohydrates) of wheat bran digested 96.7 per cent., the feces containing 0.7 per cent.

Twenty-three excrements from a number of digestion experiments made at this Station were tested for sugars in the usual way, after treating the solution with lead acetate. In twelve of them, traces of copper were reduced, corresponding to from 0.04 to 0.20 per cent. of sugars, with a mean of 0.09 per cent. This reduction is not believed to be caused by sugars, but by other reducing matters, as is plain from the following experiment: Excrement 1376, from corn silage, giving 0.15 per cent. apparent sugars; excrement 1377, from corn silage, 0.05 per cent. sugars; excrement 1411, from timothy hay, 0.20 per cent. sugars; and excrement 1437, from sorghum fodder, 0.14 per cent. sugars were taken. Fifty grams of each were digested with 500 cc. cold water, filtered, and washed with about 1000 cc. water. Basic lead acetate was added in excess, filtered, and the filtrate evaporated to about 25 cc. on a water-bath, organic matter separating. The lead was removed with sodium carbonate, filtered off, and the filtrate made up to 100 cc. Twenty-five cc., corresponding to 12.5 grams excrement, and about seventeen times as much as was used in the preliminary test, gave no trace of either sucrose or dextrose in any of the four excrements. The reducing substances probably separated during the evaporation. The traces of copper oxide were probably not due to reduction by sugars.

The twenty-three excrements were as follows: From crabgrass hay, crabgrass hay and pea-meal (2), crabgrass hay and corn bran (2), green rape (3), crabgrass hay and rice bran (2), cat-tail millet (2), sorghum fodder (2), crimson-clover hay, soja-bean silage, corn silage (4), timothy hay (2), corn fodder. In

¹ Technical Bulletin No. 4.

² This Journal, 19, 291.

the twelve materials and twenty-three experiments, sucrose and reducing sugars were completely digested.

Taking all the experiments into consideration, it is found that in thirty materials and forty-one experiments, reducing sugars are invariably digested completely, and in twenty-eight of the thirty materials, and thirty-nine of the forty-one experiments, sucrose is completely digested. The assertion that sugars are, as a rule, completely digested may be taken as established.

The determination of sugars is important with hays, and cottonseed-meal; less so in the case of the starchy foods. Hays contain a moderate amount of sugars; for example,¹ red clover (average of 21) contains 6.36 per cent., timothy hay (average of 21) 8.44 per cent., sorghum 21 per cent., corn fodder 3.9 per cent.; cottonseed-meal contains 9.22 and 7.94 per cent. raffinose, being 33.5 and 32.9 per cent. of the nitrogen-free extract, respectively. If the sugar in the hays is subtracted from the nitrogen-free extract, and then the digestibility of the latter is calculated, a considerable decrease is often found. The digestibility of nitrogen-free extract, containing sugars, is 71.8 in alfalfa hay; if sugar is subtracted, it is 68.5, a decrease of 4.6 per cent. With mixed hay, the decrease is from 55.5 to 40.4, a decrease of 27 per cent.; with timothy hay, from 60.3 to 53.5, or 11 per cent., and 56.2 to 51.1, or 9.1 per cent.; with green rape, from 93.8 to 92.5, or 1.4 per cent.; and with cottonseed-meal, from 61.5 to 42.5, the enormous decrease of 31 per cent. These figures may serve to emphasize the importance of determining sugars. The calculations and details of all these experiments are published in Bulletin No. 172 of this Station.

DIGESTIBILITY OF PENTOSANS.

The furfural produced by distillation of feeding-stuffs with hydrochloric acid comes, for the most part, from pentosans; *i. e.*, bodies which yield pentose sugars on hydrolysis. Other bodies than true pentosans are found in plants, which are decomposed with formation of furfural, such as the oxycelluloses and lignocelluloses. The latter are usually described as mixtures of cellulose and incrusting substance, or lignin.

The true pentosans are, presumably, dissolved by dilute acids

¹ E. F. Ladd: *Am. Chem. J.*, 10, 49.

and alkalies, and hence are contained in the nitrogen-free extract, but the oxycelluloses and lignocelluloses are partly attacked by these reagents also. The furfural from the crude fiber may be considered as originating from the latter bodies, to which the name pseudopentosans may be given.

W. E. Stone¹ determined the digestibility of total pentosans in a number of feeding-stuffs, titrating the furfural distillate with phenylhydrazine, and using Fehling's solution as an indicator. The per cent. of pentosans digested was found to be: in timothy hay, 48.0 and 49.5 per cent.; ditto early bloom, 60.4 and 54.6 per cent.; ditto late cut, 62.8 and 48.2 per cent.; *Danthonia spicata*, 68.6 per cent.; *Agrostis vulgaris*, 70 per cent.; *Calamagrostis canadensis* 90.4 per cent.; *Triticum repens*, 59.9 per cent.; Hungarian grass, 68.2 per cent.; *Trifolium hybridum*, 56.8 per cent.; corn fodder, northern, 76.6 per cent.; ditto southern corn, 69.6 per cent.; timothy hay and sugar-beets, 71.3 per cent.; timothy hay and rutabagas, 57.1 per cent.; timothy hay and wheat bran, 45.6 per cent.; timothy hay and gluten meal, 59.1 per cent.; *Agrostis vulgaris* and wheat bran, 54.1 per cent.; ditto and wheat middlings, 64.9 per cent. Excluding *Calamagrostis canadensis*, the average digestibility of the pentosans in the nineteen substances is 60.3 per cent., with a minimum of 45.6 and a maximum of 71.3 per cent.

J. B. Lindsay and E. B. Holland² have determined the digestibility of pentosans in the following materials: Hay of mixed grasses, (a) 63 per cent., (b) 62 per cent.; Buffalo gluten feed, 78 per cent.; new process linseed-meal, 89 per cent.; old process linseed-meal, 84 per cent.; corn cobs, 62 per cent.; dried brewer's grains, 55 per cent.; spring-wheat bran, 62 per cent.; winter-wheat bran, 64 per cent. The mean is 68.8 per cent.

H. C. Sherman³ found the digestibility of pentosans in wheat bran to be 66.2 per cent.

Determination of the total pentosans and pentosans in the crude fiber (pseudopentosans) have been made in feeding-stuffs, wastes, and excrements from digestion experiments made at this Station. The method of determining pentosans used is, in

¹ *Agr. Science*, 7, 6.

² *Ibid.*, 8, 172.

³ *This Journal*, 19, 308.

brief, as follows: Three grams of substance in a side-necked flask on a wire gauze are distilled with 100 cc. of hydrochloric acid of 1.06 specific gravity. When 30 cc. have distilled over, 30 cc. of the acid are run into the flask through a separatory funnel in such a manner as to wash down the particles on its sides. The distillation is continued in this manner until the volume of the distillate is 360 cc. A sufficient quantity of phloroglucinol to precipitate all the furfural, is added, the volume made up to 500 cc., the precipitate collected on a Gooch filter, washed with 100 cc. water, dried to constant weight at 100°, and weighed. The time required to dry the precipitate is from seven to nine hours. Commercial phloroglucinol is used, and is purified by dissolving it in hydrochloric acid of 1.06 specific gravity and allowing the diresorcinol to crystallize out.

In the case of crude fiber, three grams of material were treated, in the usual way for the determination of crude fiber using, however, 300 cc. of the acid and 300 cc. of the alkali. The fiber was then distilled with acid, as described above.

The composition of the feeding-stuffs is given in the table.

COMPOSITION OF FEEDING-STUFFS.

(Dry Matter.)

	Sugars.	Total pentosans.	Pentosans.	Pseudo- pentosans.	Residual N-free extract.
Timothy hay No. 1.....	8.33	24.86	19.71	5.15	16.88
Crabgrass hay No. 1.....	1.89	26.25	21.90	4.35	21.40
Crabgrass hay No. 2.....	2.20	24.71	19.85	4.85	24.09
Cowpea-meal.....	5.66	6.83	6.83	0	52.20
Corn bran.....	2.93	25.15	25.15	0	41.36
Green rape No. 1.....	8.41	10.57	9.57	1.00	29.81
Green rape No. 2.....	7.03	8.71	8.04	0.67	26.04
Rice bran.....	1.56	10.88	9.88	1.00	40.31
Cottonseed-meal.....	7.94	7.83

The pentosans in the crude fiber is, in timothy hay No. 1, 20.7 per cent. of the total pentosans; in timothy hay No. 2, 20.5 per cent.; in crabgrass hay No. 1, 18.4 per cent.; in crabgrass hay No. 2, 19.6 per cent.; in cowpea-meal and corn bran, none; in green rape No. 1, 9.5 per cent.; in green rape No. 2, 7.7 per cent., and in rice bran, 9.2 per cent. It is apparent that the crude fiber of hays contains a large percentage of the pentosans. The pentosans are distributed between the crude fiber and the nitrogen-free extract. The pentosans in the crude fiber

are not here regarded as true pentosans, but are called pseudopentosans; they are different from the pentosans in the nitrogen-free extract, although the line of separation between the two is an arbitrary one. The distribution and digestibility of the pentosans are given in the table. It is seen that from 0 to 21 per cent. of the pentosans are pseudopentosans, and that in four of the five cases the pseudopentosans are less digestible than the pentosans in the nitrogen-free extract. The digestibility of the total pentosans varies from 53 to 95 per cent.

DISTRIBUTION AND DIGESTIBILITY OF PENTOSANS.

	Of 100 parts pentosans		Digestibility of pentosans.		
	True	Pseudo-	Total	True	Pseudo-
Timothy hay No. 1.....	79.3	20.7	55.8	58.1	46.9
Timothy hay No. 2.....	79.5	20.5	55.9	57.0	52.0
Crabgrass hay No. 1.....	81.6	18.4	63.1	61.0	69.9
Crabgrass hay No. 2.....	80.4	19.6
Cowpea-meal ¹	100.0	0	76.1	76.1
Corn bran ¹	100.0	0	71.6	71.6
Green rape No. 1.....	90.5	9.5	94.6	95.7	84.6
Green rape No. 2.....	92.3	7.7	91.9	93.2	75.9
Rice bran ¹	90.8	9.2	53.5	57.3

DIGESTIBILITY OF NITROGEN-FREE EXTRACT.

The composition and digestibility of the nitrogen-free extract is given in the table below. The residual nitrogen-free extract is the total nitrogen-free extract less sugars and pentosans. It varies in quantity from 47 to 85 per cent. of the nitrogen-free extract.

COMPOSITION AND DIGESTIBILITY OF NITROGEN-FREE EXTRACT.

	In 100 parts			Digestibility.	
	Sugars.	Pentosans.	Residue.	Pentosans.	Residue.
Timothy hay No. 1.....	14.9	35.2	49.9	58.1	50.1
Timothy hay No. 2.....	10.5	41.6	47.9	57.0	46.0
Crabgrass hay No. 1....	4.2	48.4	47.4	61.0	32.7
Crabgrass hay No. 2.....	4.8	43.0	52.2
Cowpea-meal ²	4.8	10.6	84.6	76.1	97.4
Corn bran ²	4.2	36.2	59.6	71.6	86.1
Green rape No. 1.....	15.2	20.6	64.2	95.7	91.4
Green rape No. 2.....	19.8	18.9	61.3	93.2	86.5
Rice bran ²	3.0	19.1	77.9	57.3	85.0

¹ Calculated from ration with crabgrass hay.

² Digestibility calculated from ration with crabgrass hay.

In the timothy hays, the crabgrass hay, and the green rape, the order of digestibility is: sugars, pentosans, residue. In the cowpea-meal, the corn bran, and the rice bran, the order is: sugars, residue, pentosans, but this residue consists most largely, if not entirely of starch, so that we may say that starch is more digestible than pentosans. The order of digestibility of the components of the nitrogen-free extract is, then,—sugars, starch, pentosans, and residue.

DIGESTIBILITY OF CRUDE FIBER.

Crude fiber contains from 0 to 21 per cent. of the total pentosans, sometimes as much as 42 per cent.¹ The table below exhibits the composition and digestibility of the crude fiber. In four of the five cases, the pseudopentosans are less digested than the residue, and the residue more so than the total crude fiber, although the difference is not great. The digestibility of the residual nitrogen-free extract has been placed in the table for purposes of comparison. With timothy hay, and crabgrass hay, it is less digestible than the residual crude fiber, in one case more, the other two less, digestible than the pseudopentosans. With the green rape, its digestibility is slightly greater than that of the residual crude fiber. With the starchy foods, its digestibility is greater, as a matter of course, since it consists for the most part of starch.

COMPOSITION AND DIGESTIBILITY OF CRUDE FIBER.

	In 100 parts		Digestibility.			Residual nitrogen-free extract
	Pseudo-pentosans.	Residue.	Total.	Pseudo-pentosans.	Residue.	
Timothy hay No. 1	9.2	90.8	52.3	46.9	53.3	50.1
Timothy hay No. 2	14.4	85.6	53.8	52.0	54.1	46.0
Crabgrass hay No. 1	13.0	87.0	67.3	69.9	67.0	32.7
Crabgrass hay No. 2	13.4	86.6	62.5 ²
Cowpea-meal ³	0	100.0	39.2	39.2	97.4
Corn bran ¹	0	100.0	50.8	50.8	86.1
Green rape No. 1	7.7	92.3	90.0	84.6	90.4	91.4
Green rape No. 2	6.3	93.7	84.0	75.9	84.6	86.5
Rice bran ¹	8.3	91.6	19.1	19.1	85.0

While, therefore, the order in the series, sugar, starch, pentosans, and residual nitrogen-free extract, is subject to little doubt,

¹ J König: *Landw. Versuch. Stats.*, 48, 93.

² Calculated from ration with crabgrass hay.

³ Calculated from ration with cowpea-meal.

and the order, residual crude fiber, pseudopentosans, is not doubtful, the combination of the two series is more doubtful. The approximate arrangement in the order of digestibility would be sugar, starch, pentosans, residual crude fiber, residual nitrogen-free extract, pseudopentosans, the position of residual crude fiber and pseudopentosans being subject to change.

It is seen that the residual nitrogen-free extract, in three hays at least, is less digestible than the residual crude fiber. Is this an actual or an apparent difference? It is assumed in digestion experiments that those fodder groups which are not digested pass through unchanged, an assumption that must be modified for the nitrogenous matters and the ether extract, since products of metabolism appear in the excrement which fall into these two groups. It is quite possible that crude fiber undergoes some change that renders it soluble in acids or alkalies.

Crude fiber may disappear :

- (1) By formation of soluble compounds and resorption ;
- (2) By decomposition to carbon dioxide and marsh gas ;
- (3) By decomposition with the formation of carbon dioxide and marsh gas, and soluble products which are resorbed ;
- (4) By decomposition with formation of products which are not resorbed, and are soluble in hot acids or alkalies, hence goes into the nitrogen-free extract.

Besides the sugars, starches, gums, etc., the nitrogen-free extract of hays is composed of the less resistant portions of the cell walls, partly made up of pentosans. Our digestion experiments seem to show that the older and more resistant cellular structures (crude fiber) are in many cases digested to a greater extent than the younger and less resistant. To avoid this difficulty, it has been assumed that the more resistant portions are converted by bacteria into gases and soluble products, which are resorbed. This may be part of the truth, but not all of it. We would naturally suppose the less resistant portions—in the nitrogen-free extract—to be attacked by the bacteria first, and the nitrogen-free extract ought to be digested more completely than the crude fiber. The explanation that seems probable is, that the crude fiber and undigested nitrogen-free extract, remaining several days in the intestines under very favorable conditions for the action of micro-organisms, are decomposed, with formation

of gases, of soluble products which are resorbed, and of insoluble products which pass into the excrement, and, being soluble in acids or alkalies, appear in the analysis as nitrogen-free extract. The digestibility of the nitrogen-free extract would appear less than it really is, and that of the crude fiber, greater.

ANALYSIS OF FEEDING-STUFFS.

This work has shown that if we take the sugars, starch, and pentosans from the nitrogen-free extract, the residue is sometimes more, sometimes less digestible than the crude fiber, and often the difference is not great. For this reason, in the analysis of feeding-stuffs, it is of more importance to determine sugar, starch, and pentosan, than to determine crude fiber.

E. Schulze¹ has proposed that, in addition to the determination of crude fiber, the non-nitrogenous matters insoluble in ether, alcohol, water, and diastase solution be determined. The residue would consist of the material of cell walls, insoluble proteids, and a portion of the ash. It is corrected for the ash and proteids. This method should not be used in digestion work, since insoluble nitrogen-free extract or crude fiber may have become soluble during its several days' stay in the animal. It may be used when a knowledge of the properties of a feeding-stuff is desired quickly.

SUMMARY.

1. Sugars are found in all feeding-stuffs, are completely digested, as a rule, and their determination is of especial importance in the case of hays and cottonseed-meal.
2. The average digestibility of pentosans in thirty-four samples is 64.2. The average for timothy hay (eight samples) is 53.9.
3. The constituents of the nitrogen-free extract may be arranged in the following order according to their digestibility: (1) sugars, (2) starch, (3) pentosans, (4) residue.
4. The pseudopentosans of crude fiber are less digestible than the residue. The residue is sometimes more, sometimes less digested than the residual nitrogen-free extract.
5. Crude fiber may be changed during digestion so as to appear as nitrogen-free extract in the excrement.
6. The determination of sugar, starch, and pentosans is more important than that of crude fiber.

May, 1900.

¹ *Landw. Versuch.-Stats.*, 49, 434.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF
APPLIED SCIENCE, No. 34.]

ON THE HYDROCARBONS IN HEAVY TEXAS PETROLEUM.¹

BY CHARLES F. MABERY AND D. M. BUCK.

Received June 15, 1900.

THE heavy petroleums that hitherto have been looked on as only fit for fuel are capable, if properly refined, of yielding valuable products. This is especially true of the deposits recently exploited in Wyoming, Texas, and in other sections. The Corsicana oil in Texas has been shown by Mr. Clifford Richardson to yield an oil that may be refined into gasoline, burning oil, and other products ordinarily obtained from light petroleums. Large areas of oil territory have recently been developed in Texas that yield oils of higher specific gravity, and that are of value for what they contain of the higher products. The rapid development of Texas oil territory bids fair to advance the state into an equivalent place with California as oil-producing territory.

As to the hydrocarbons which compose the heavy Texas oil, nothing whatever has hitherto been known. It is practically impossible to separate any of its constituents by the ordinary method of distillation. This examination of the Texas oil was undertaken with the purpose of ascertaining the principal series of hydrocarbons which compose the crude oil.

The specimen was obtained from a large territory owned by the Forward Reduction Company, of this city. The crude oil was very thick and dark in color. Its specific gravity at 20° was 0.9500. A determination of sulphur by the Carius method gave 0.94 per cent. These heavy oils almost invariably contain water suspended, and it is almost impossible to remove the water by drying, and the oil can not be distilled while it contains water on account of violent bumping. Under atmospheric pressure, scarcely any of the oil distilled below 240°. After drying by standing a long time in a warm place with fused calcium chloride, when distilled in vacuo under 13 mm. pressure, the distillates collected in the following proportions and gave the specific gravity annexed:

¹ The work in this paper was the subject of a thesis by Mr. Buck for the degree of Bachelor of Science.

150°	150°-230°	230°-300°	Above 300°
10 per cent.	32 per cent.	21 per cent.	37 per cent.
0.8753	0.9222	0.9602	Very thick.

Next 500 grams were distilled under 25 mm. up to 310°, leaving a residue in the flask of 175 grams. The distillations were repeated several times until larger quantities collected at the following temperatures:

125°-130°	140°-145°	160°-165°	175°-180°	195°-200°	215°-220°
0.8744	0.8848	0.8986	0.9095	0.9231	0.9373
	225°-230°	240°-245°	270°-275°		
	0.9432	0.9478	0.9559.		

For the removal of benzene hydrocarbons and other impurities, the constituents with lower boiling-points were treated several times with fuming sulphuric acid, then washed with sodium hydroxide and water. The remaining oil was nearly colorless. In order to prevent decomposition of the less stable constituents with higher boiling-points by the fuming acid, the heavy oil was dissolved in light gasoline. After the solution became colorless, the gasoline was distilled off, leaving the heavy oil. By this method, it is possible to purify any of the distillates with high boiling-points without decomposition.

The fraction 125°-130° (25 mm.), after treatment with the fuming acid, gave as its specific gravity 0.8711, very little less than the specific gravity of the unpurified distillate, indicating that very little else was contained in this fraction but the principal hydrocarbon. A determination of the molecular weight of the oil at the freezing-point of benzene gave 196; required for $C_{14}H_{28}$, 194. The index of refraction was also determined and the molecular refraction calculated from it was 62.39; required for $C_{14}H_{28}$, 62.34. A combustion of the oil gave 86.56 per cent. of carbon, and 13.46 per cent. of hydrogen; required for $C_{14}H_{28}$, carbon 86.59, hydrogen 13.41.

The fraction 140°-145° (25 mm.) was purified in the same manner, and the same determinations were made. The results of the determinations of carbon and hydrogen, molecular weight determinations and molecular refraction led to the formula of the hydrocarbon $C_{16}H_{32}$.

By the same method of purification, the fraction 160°–165° (25 mm.) was obtained nearly colorless, and it then gave as its specific gravity 0.8894, only slightly less than the specific gravity of the unpurified oil. Determinations of carbon and hydrogen, of its molecular weight and molecular refraction, gave results leading to the formula $C_{16}H_{30}$.

After treatment with the fuming acid, the fraction 175°–180° (25 mm.) gave as its specific gravity 0.8966, essentially the same as that of the unpurified oil. The formula established by the same determinations as the others was $C_{17}H_{32}$.

The specific gravity of the fraction 195°–200° (25 mm.), after purification with fuming sulphuric acid, was 0.9070. Determinations of carbon and hydrogen, and molecular weight, led to the formula $C_{19}H_{34}$, although the low percentage of hydrogen indicated that the distillate contained some of the hydrocarbon with less hydrogen. The distillate 215°–220° (25 mm.) gave as its specific gravity, after purification, 0.9163. Its formula, established by analysis and determination of molecular weights, is $C_{21}H_{36}$.

The fraction 240°–245° (25 mm.) gave as its specific gravity 0.9306. No other determinations were made of this oil than its molecular weight, which corresponded to the formula $C_{23}H_{38}$. The fraction 270°–275° (25 mm.) was extremely viscous, and could be purified only by dissolving in gasoline. It gave a clear, slightly yellow oil, with a specific gravity 0.9410, practically the same as the unpurified distillate. Determinations of carbon and hydrogen, of molecular weight and molecular refraction, corresponded to the formula $C_{25}H_{40}$.

It appears, therefore, that this heavy Texas oil contains hydrocarbons from $C_{14}H_{28}$ to $C_{19}H_{34}$ of the series C_nH_{2n-2} , and higher hydrocarbons $C_{21}H_{36}$ to $C_{25}H_{40}$ of the series C_nH_{2n-4} . From the slight changes in specific gravity after thorough agitation with fuming sulphuric acid, it appears that these condensed methylenes constitute the chief body of the crude oil which distills within these limits. The first series is satisfied by assuming that the molecule is composed of two methylene rings connected in the same manner as diphenyl, with a sufficient number of methyl side-chains to account for the formula or with connecting carbon atoms between the rings. The study of the constituents

of Texas, California, and Canadian petroleum, with high boiling-points, is now in progress.

A summary of the results obtained in the examination of this petroleum is given in the following table :

	B. P. (25 mm.)	Sp. gr.	Index of refraction.	Molecular refraction	
				Calculated.	Found.
$C_{14}H_{28}$	125°-130°	0.8711	1.4713	62.34	62.39
$C_{15}H_{32}$	140°-145°	0.8788	1.4746	66.94	66.70
$C_{16}H_{36}$	160°-165°	0.8894	1.4672	71.55	69.40
$C_{17}H_{40}$	175°-180°	0.8966	1.4721	76.14	73.85
$C_{18}H_{44}$	195°-200°	0.9020	1.4928	85.35	84.70
$C_{21}H_{58}$	215°-220°	0.9163	1.4979	92.46	92.91
$C_{25}H_{70}$	270°-275°	0.9410	1.5152	110.87	111.00

[CONTRIBUTION FROM THE LABORATORY OF HYGIENE, UNIVERSITY OF PENNSYLVANIA.]

AN EXPERIMENTAL STUDY OF THE GAS-PRODUCING POWER OF BACILLUS COLI COMMUNIS UNDER DIFFERENT CONDITIONS OF ENVIRONMENT.

BY MARY ENGLE PENNINGTON AND GEORGE C. KÜSEL.

Received June 29, 1900.

THE power which some bacteria possess of liberating certain gaseous elements and compounds from suitable culture media has been the subject of a number of investigations. These investigations have brought to light many interesting facts, and have established methods of diagnostic value based upon gas production. Dr. Theobald Smith, in the account of his now classic experiments upon fermentation, has given a number of species which produce gases, the necessary conditions, quantity of gas produced, etc. Various analyses are on record, also, of the gas liberated, these analyses being more or less detailed depending upon the point of view of the investigator and the time when the work was done. Among the earlier workers we find, generally, that they were content with the determination of the amount of carbon dioxide. The residual gas, being found to be explosive, was accepted as hydrogen.

Later studies have been made with more care, and in consequence the presence of other gases has been recognized. Pammel and Bennett¹ have studied the action of several gas-producing organisms with especial attention to their behavior toward

¹ This Journal, 18, 157 (1896).

different sugars; namely, glucose, cane-sugar, and lactose. They mention the fact that the first portions of escaping gas are nearly pure hydrogen, but are inclined to ascribe this to the absorptive power for carbon dioxide possessed by the medium. The culture period for each experiment is given, and the analytical data, obtained by growing the organisms in various media, are compared, but nothing further regarding the progressive alteration in the composition of the gas formed is noted.

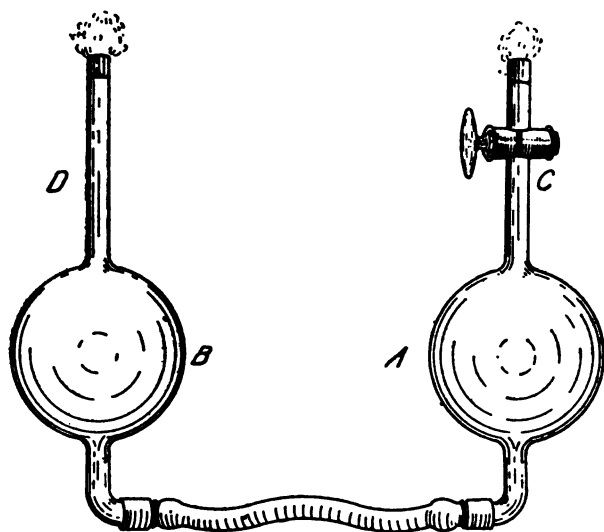
Some fermentation work with *Bacillus coli communis* which has been done in this laboratory, led us to believe that a change in the composition of the gas does occur with the advancing age of the culture and, also, that appreciable quantities of gases other than hydrogen and carbon dioxide are formed. The work in this laboratory also indicated that gas production by *Bacillus coli communis* in glucose bouillon in the usual saccharimeter tube is not so constant, either in relation to time of gas production or of the amount produced, as is generally believed. It seemed advisable, therefore, to cultivate this organism under the most concordant conditions possible, and to submit the gases produced to a careful chemical examination.

The chemist who undertakes quantitative chemico-bacteriological work has found in the past, and still finds, a source of error which at present seems insurmountable. This error lies in the quantity and quality of the inoculating material. Wherever inoculations are to be made the most careful work of trained eyes and skilled hands may yet leave a margin, plus or minus, of untold thousands of organisms, for with cells so prolific as are bacteria a small difference to-day is enormous to-morrow. Not only, too, must we consider the number of active organisms produced, but the waste products of those cells which are already dead may exert an appreciable influence upon later comers.

The gas-producing ability certainly varies considerably with the age of the culture. Many trials have demonstrated that *Bacillus coli communis* made upon nutrient agar are most active, so far as gas production is concerned, when three days old, the organisms having been kept at a temperature of 37° C. Older cultures, as a rule, produce less gas. This may be due to a decreased vitality of the germ from lack of food supply or from noxious waste products. In all of the experimental work given

below a three days' slant culture on agar was used as the seeding material.

After many trials with the various forms of apparatus for the collection and isolation of the gases generated by bacteria the following method was devised and used exclusively. The advantage of this form of apparatus is that it is easily handled, cleaned, and sterilized, besides being perfectly tight. That it is



exceedingly simple will be seen from the accompanying diagram. *A* is a glass bulb of 250 cc. capacity having an inlet, *C*, three inches long, into which a glass stop-cock is fused and an outlet *D*, of the same length, bent at right angles about one inch below the bulb. *B* is a like bulb except that the stop-cock is omitted. Heavy walled rubber tubing connects these two bulbs and is closely wired, both outlets being roughened to facilitate this. The inlets are plugged with cotton-wool, when the apparatus may be sterilized in an autoclave.

In the experiments to be described exactly 250 cc. of the desired culture medium were admitted through *D* the stop-cock of *C* being open. The level was then adjusted until the bore of the stop-cock was just filled. The cock was turned, and the apparatus, so far as *A* was concerned, was tight. Resterilization

in an autoclave at 45 pounds' pressure rendered the apparatus fit for inoculation. This was performed either by slipping a platinum wire through the stop-cock bore until it met the medium, or, as we preferred, by placing a definite number of drops of a suspension culture in the inlet tube *C* and drawing them into the bulb by lowering *B*.

As the organisms multiply, the gas collects in *A* displacing the liquid and forcing it over into *B*. The flexible connection between the two bulbs enables one to readily adjust the levels so that undue pressure, which checks fermentation, is obviated. The bulbs have been allowed to stand for days with bulb *B* depressed to its fullest extent but not the slightest inward leakage has been detected. When the experiments were being conducted a slight pressure in *A* was maintained as an additional precaution, so that the leak, if any, should be outward.

All the experiments were conducted at an incubator temperature, 37° C. The media were made with the greatest exactness possible. Commercial peptone, glucose, and salt were carefully dried and weighed accurately. When bouillon was desired Liebig's "*Extractum Carnis*" was used. The reaction of the medium was always neutral at the beginning of the experiment. Tenth-normal sodium hydroxide was used for this neutralization, phenolphthalein being the indicator. The gases were withdrawn from the bulb after cooling the latter to 18° to 19° C. and analyzed over mercury in a Hempel apparatus. Hydrogen was determined by explosion with oxygen. Hydrocarbons were determined by residual carbon dioxide. Nitrogen was found by difference. Heavy hydrocarbons were sought, but were not detected. All results are expressed in percentages. The amount of gas produced did not, as a rule, permit of more than one accurate carbon dioxide analysis. After absorbing the carbon dioxide, however, duplicate determinations of hydrogen, nitrogen, and methane were made. To exclude the personal error all the analyses were made by one person. When the variation in the results were large the experiments were submitted to a bacteriological investigation, but the cultures were found to be pure.

NITROGEN AND METHANE.

A series of bulbs were filled as above described with neutral

bouillon containing 1 per cent. peptone, 0.5 per cent. sodium chloride, 0.5 per cent. Liebig's beef extract, and 1.5 per cent. glucose. The individual bulbs were analyzed at the expiration of the periods indicated in the table.

TABLE I.

Series 1.

No.	Duration of experiments. Hours.	Carbon dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1....	72	26.6	65.3	4.30	3.8	93
2....	72	26.45	65.82	3.61	4.12	64
3....	144	28.48	65.83	1.13	4.56	80
4....	168	23.75	70.13	1.15	4.97	67.8
5....	192	23.59	69.88	2.38	4.95	85

Series 2.

1....	36	34.30	63.20	1.00	1.30	82
2....	60	33.83	62.69	1.86	1.62	93.4
3....	84	27.03	69.88	1.02	2.07	83

Series 3.

1....	48	34.00	63.00	1.5	1.5	93
2....	72	27.5	66.3	3.00	3.2	98
3....	120	28.00	66.5	2.00	3.5	90

According to Table I, in addition to the carbon dioxide and hydrogen, the gases usually present, we find also nitrogen and methane. These gases were invariably found, and their presence in such appreciable quantities is of interest. Grimberty¹ has cultivated *Bacillus coli communis* in the presence of amido bodies, nitrates and nitrites, and states that amides are necessary if denitrification processes are to continue. In Grimberty's experiments sugar was not mentioned, the study being made in nitrated, or amidated, peptone solutions exclusively. In Bennett and Pammel's work we find no mention of nitrogen or methane in the gas produced. Wolff,² in a recent paper on denitrification, states that this organism reduces a nitrated peptone—glucose medium, giving nitrites.

Frequent repetition of our experiments, where no nitrates were added, with every possible precaution against admixture of air, gave invariably some nitrogen. The question therefore arose: Does the presence of air in bulb *B* affect the nitrogen production?

¹ *Ann. d. P. Inst.*, Pasteur, 13, 67 (1889).

² *Hygien. Rundsch.*, 9, 1169.

While fermentation is active the tendency would be to carry the organisms out of the field of activity (bulb *A*) and a backward migration cannot be very extensive. But at the close of the active period the organisms in *B*, may find their way into *A* again. Do they, from their contact with the oxygen at the surface of the liquid in *B*, become so modified physiologically that they alter the usual course of fermentation? To determine this point the following experiments were made in which all oxygen was excluded.

The apparatus above described was filled and sterilized in the usual manner. A Geissler potash bulb containing a freshly prepared pyrogallol and sodium hydroxide solution was attached to *B*, and a wash-bottle rigged flask, containing a like solution, was attached to *A*; the stop-cock was then opened, the level of *A* raised and the liquid allowed to flow into *B*, until the bulb was quite full. The air entering *A* was, of course, deprived of oxygen by the pyrogallate in the wash-bottle flask. The relative levels were next altered and bulb *A* refilled. The air in *B* was free from oxygen and remained so as indicated by testing over active phosphorus. The gas produced under such conditions still showed nitrogen, but we were surprised to find that hydrocarbons had disappeared (see Table II).

TABLE II.

Series 1.

No.	Duration of experiment. Hours.	Carbon dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1.....	40	30.00	67.80	2.20	82.0
2.....	64	28.91	67.53	3.56	83.0
3.....	86	28.00	66.99	5.01	83.2

Series 2.

1.....	22	34.70	63.58	1.72	83
2.....	36	36.80	60.10	3.10	97
3.....	64	36.00	59.18	4.82	94

Series 1 and 2 of Table II were made with glucose bouillon of the composition given, and, except that the series were started on different days, were as exactly alike as possible. The results show well the marked variation which frequently appears, and which will be again met with in the course of this paper.

Control bulbs without the pyrogallate tubes were made in each case, and the analyses always showed hydrocarbons to be present. Hence we find that the entire exclusion of oxygen does not modify the nitrogen production in the least but that under such circumstances hydrocarbons are not produced.

In the foregoing experiments the organisms had a large supply of amido nitrogen on hand in the form of meat extractives. They had, also, the proteid nitrogen of the peptone. Commercial peptone varies considerably in composition and contains always more or less amido nitrogen. If the organisms are able to reduce the nitrogen of the extractives only we would expect to find much less nitrogen in a peptone-glucose solution than in one containing meat extractives in addition to the other constituents.

To determine to what extent these added meat extractives enter into the nitrogen evolved, the following series of bulbs were made with a culture medium composed of 1 per cent. peptone (Witte's) containing 1.5 per cent. glucose and 0.5 per cent. salt. The pyrogallate bulbs were not attached.

TABLE III.

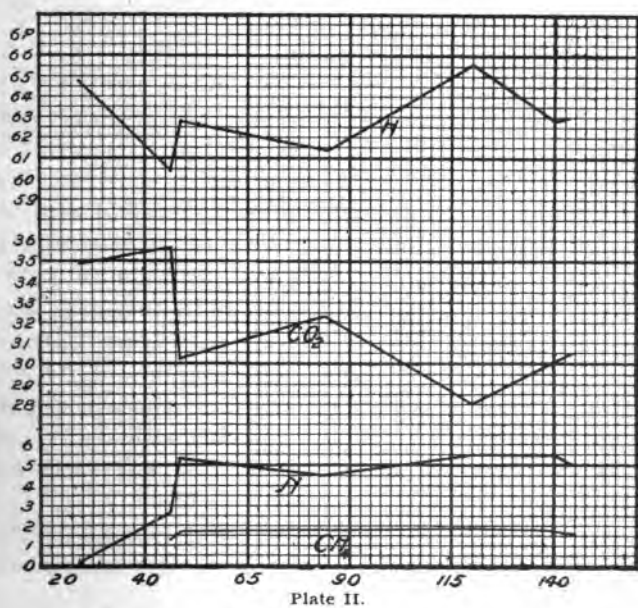
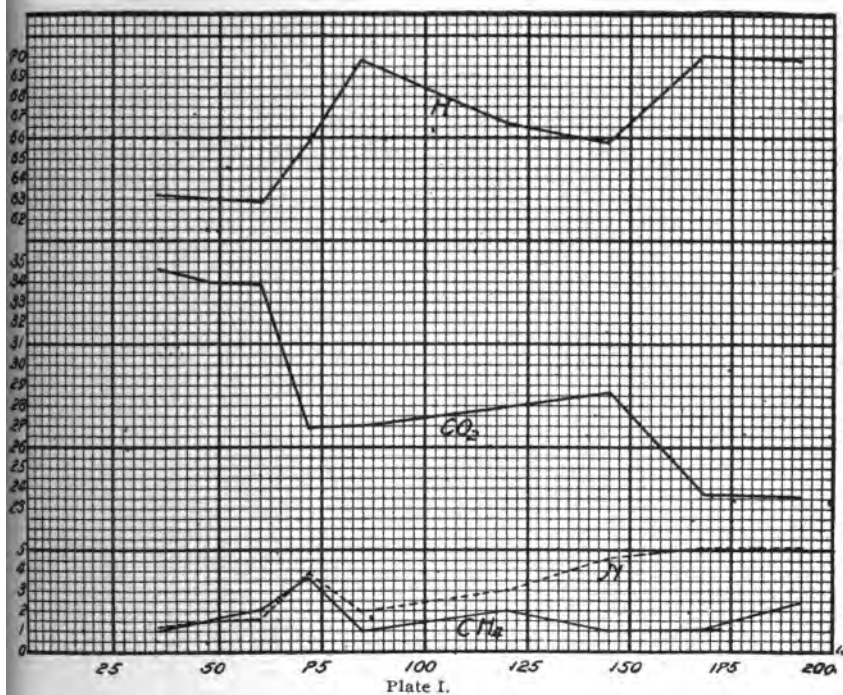
Series 1.

No.	Duration of experiment. Hours.	Carbon. dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1....	24	34.80	65.11	0.09	100.0
2....	48	30.2	62.83	1.63	5.34	97.4
3....	120	28.11	64.6	1.80	5.49	86.0

Series 2.

1....	46	35.58	60.34	1.34	2.74	97.8
2....	84	32.00	61.39	1.00	4.54	94.8
3....	140	30.00	62.72	1.78	5.50	98.0
4....	144	30.41	62.88	1.77	4.94	96.0

Bulb No. 1 of Series 1, Table II, is the only experiment in which we have failed to detect nitrogen in appreciable amounts. It will be noticed that this bulb also lacks methane. The experiment was carried out in strict accord with the other members of the series, the medium being the same preparation, the inoculation from the same suspension culture. The reason for this variation is unexplained.



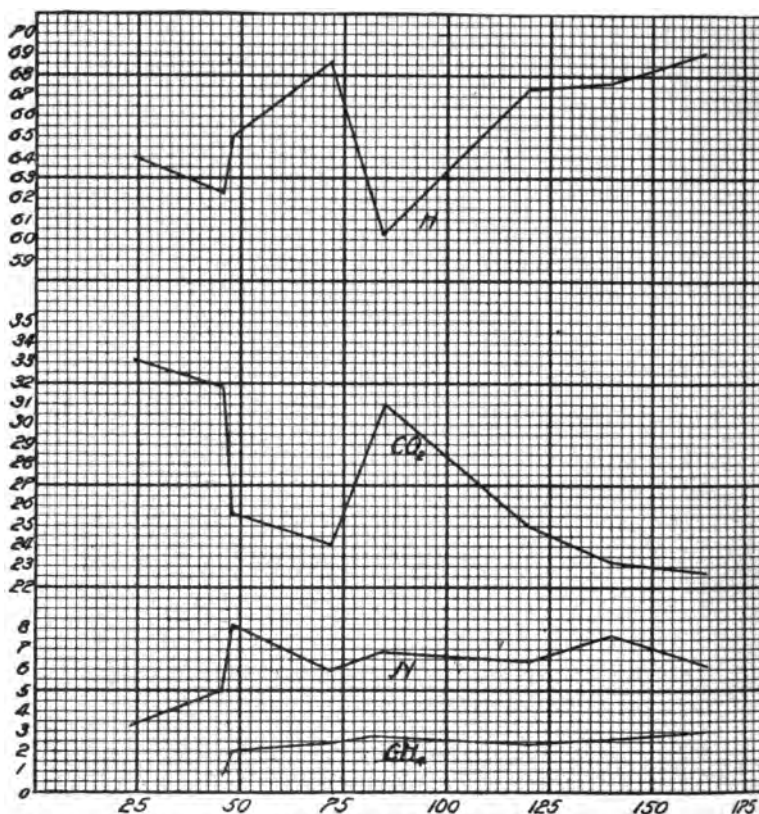


Plate III.

A comparison of the nitrogen obtained with and without the addition of extractives shows no appreciable nitrogen difference. If the amido nitrogen only is liberated we have in bulb 4 of Series 2 a quantity of nitrogen corresponding to 0.0184 gram of creatine. According to Allen,¹ Liebig's *Extractum Carnis* contains 29.32 per cent. meat bases. As 5 grams of the extract were added to 1 liter of the medium we have about 1.46 gram of extractives; or, as each bulb was supplied with 250 cc. of the fluid, 0.366 gram was available in each experiment. A very small quantity of amido nitrogen then is split off.

Because of the variability of peptones of different makes another sample, one obtained from Merck, was subjected to experiment.

¹ "Commercial Organic Analysis," Vol. IV, p. 311.

After careful drying it was made into a 1 per cent. solution containing salt and glucose as before. As in the similar experiments with Witte's peptone, extractives were omitted.

TABLE IV.

<i>Series 1.</i>						
No.	Duration of experiment. Hours.	Carbon dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1.....	24	33.41	64.07	...	2.52	52.0
2.....	48	25.77	64.98	2.00	7.25	50.0
3.....	72	24.16	68.60	2.18	5.06	57.0
4.....	120	24.89	67.36	2.35	5.40	53.0
<i>Series 2.</i>						
1.....	46	31.80	62.33	1.93	3.94	47.6
2.....	84	31.06	60.33	2.77	5.84	93.6
3.....	140	23.15	67.69	2.60	6.56	50.0
4.....	164	22.69	69.10	3.10	5.11	57.6

With this sample of peptone there was a marked fall in the amount of gas produced, only about one-half the usual quantity being obtained. Bulb 1, of Series 1, Table IV, had made no methane at the end of twenty-four hours, but at the expiration of forty-eight hours, 2 per cent. was present in No. 2. The amount of carbon dioxide is distinctly less than that usually found.

VARIATION IN AMOUNT OF GASES PRODUCED.

A study of the results which have been obtained discloses an interesting relation from the standpoint of time variation. Table I, Series 1, 2, and 3, were made under conditions as concordant as possible and should therefore be comparable. Uniting these three tables into one we get the following :

TABLE V.

No.	Duration of experiment. Hours.	Carbon dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1.....	36	34.50	63.20	1.00	1.30	82.0
2.....	48	34.00	63.00	1.5	1.50	93.0
3.....	60	33.83	62.69	1.86	1.62	93.4
4.....	72	26.6	65.3	4.30	3.80	98.0
5.....	72	27.5	66.3	3.00	3.20	98.0
6.....	72	26.45	65.82	3.61	4.12	64.0
7.....	84	27.03	69.88	1.02	2.07	83.0
8.....	120	28.00	66.5	2.00	3.05	90.0
9.....	144	28.48	75.83	1.13	4.56	80.0
10.....	168	23.75	70.13	1.15	4.97	67.0
11.....	192	23.59	69.88	2.38	4.95	65.0

There is here a marked difference in the quantitative relations of the various gases according, apparently, to the age of the culture. Charting these results, Plate I, we get a curve which at the end of thirty-six hours shows a maximum quantity of carbon dioxide. Seventy-two hours shows a decrease in carbon dioxide with a corresponding gain in hydrogen. During both of these periods the nitrogen and methane increase slowly but steadily, and are about equal in amount, the only exception being No. 5, eighty-four hours, in which there is a marked absence of both these gases. The third period is marked by a second rise in the amount of carbon dioxide, which is, however, slight, the hydrogen remaining about stationary. The methane now falls behind but the nitrogen is increased, an increase which is maintained in the last period, though here the carbon dioxide is reduced to a minimum and the hydrogen rises to a maximum.

Uniting the series under Table III, and Table IV, we get Tables VI and VII (Plate II and III), where we find that the same principle holds good, though the length of time occupied by the different stages is not exactly the same in all cases.

TABLE VI.

No.	Duration of experiment. Hours.	Carbon dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1.....	24	34.80	65.11	0.09	100.0
2.....	46	35.58	60.34	1.34	2.74	97.8
3.....	48	30.2	62.83	1.63	5.34	97.4
4.....	84	32.27	61.39	1.80	4.54	94.8
5.....	120	28.11	64.6	1.80	5.49	86.8
6.....	140	30.00	62.72	1.78	5.50	98.0
7.....	144	30.41	62.88	1.77	4.94	96.0

TABLE VII.

No.	Duration of experiment. Hours.	Carbon dioxide. Per cent.	Hydrogen. Per cent.	Methane. Per cent.	Nitrogen. Per cent.	Total volume. cc.
1.....	24	33.41	64.07	2.52	52.2
2.....	46	31.80	62.33	1.93	3.94	47.6
3.....	48	25.77	64.98	2.00	7.25	50.00
4.....	72	24.16	68.60	2.18	5.06	57.00
5.....	84	31.06	60.33	2.77	5.84	39.6
6.....	120	24.89	67.36	2.35	5.40	53.00
7.....	140	23.15	67.69	2.60	6.56	50.00
8.....	164	22.69	69.10	3.10	5.11	57.6

There seems to be, on the whole, an intimate relation between the reducing power which liberates hydrogen and that which liberates nitrogen. Carbon dioxide is generated in greatest quantity at the outset, when, perhaps, the available oxygen is most plentiful and poisonous waste products are in smallest proportion. The reducing power gains strength in the latter stages, when the conditions for carbon dioxide production are not favorable. If, as some investigators maintain, the denitrifying ability of *Bacillus coli communis* is due to a secondary action rather than to a primary one, the rise in carbon dioxide after gas production has been maintained for some hours may be accounted for on the supposition that those substances produced by the organism which liberate nitrogen have, through the reaction involved in that liberation, been so altered that their toxicity for the bacteria is, in part at least, removed. The carbon dioxide function then asserts itself, producing again products which are hurtful. These, combined with those already present, resolutely check the liberation of carbon dioxide. The hydrogen-producing function, as well as the nitrogen, can still maintain its existence for a time, thereby raising the relative proportions of those gases.

We believe that the irregularity of the foregoing results, even when made with the greatest care that we could bestow, is worthy of consideration. For the very great majority of these variations we can offer no definite explanations. It seems to us that refinement in manipulation brings to view variations which can only be due to life conditions, to cope with which our methods are incalculably clumsy. Until these methods are improved the quantitative chemistry of the living cell cannot progress very far, and it is with the plea for further work along these lines that this communication is made.

[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 38. SENT BY H. W. WILEY.]

THE ADULTERATION AND ANALYSIS OF THE ARSENICAL INSECTICIDES.

BY J. K. HAYWOOD.

Received July 6, 1900.

IN the following paper I will first give a résumé of what has been done in the analysis of insecticides, showing which are usually pure and which often adulterated, and laying particular stress on the arsenical insecticides, which are of the most importance now on the market. This will be followed by a series of carefully-tested methods for the analysis of the more common insecticides, with the results indicated.

Various groups of insects act harmfully on plants and require special methods of treatment to kill them. Among these classes of insects may be mentioned subterranean insects, household pests, animal parasites, internal feeders, etc. The insects which principally injure plants, however, and for which insecticides are usually applied, are external feeders, which include "biting" and "sucking" insects.

For the first, or "biting" insects, some substance is used which can be sprayed on the parts of the tree attacked, and then eaten by the insect with its food. Such substances are Paris green, Scheele green, London purple, lead arsenate and arsenite, barium arsenite, arsenious oxide, etc.

For the second group, or "sucking" insects, substances must be used which will act externally on the bodies of the insects and smother them either by closing their pores or filling the air around with poisonous vapors. Among the latter insecticides may be mentioned insect powder, sulphur, kerosene, hydrocyanic acid, carbon disulphide, ammonia, formalin, etc. Experience has proved that a great many of the insecticides mentioned above are nearly always pure as they occur in commerce. There are certain ones, however, which often show adulteration, among them being cupric carbonate (impure because of faulty methods of manufacture), potassium cyanide, potash lye (which is often sodium hydroxide), formalin (which should be a 40 per cent. solution of formaldehyde, but often is not), and most of the arsenical preparations.

I will not attempt to go into the adulteration of all the articles mentioned above, but will lay particular stress on the adulteration of the arsenicals. These include Paris green, Scheele green, London purple, arsenious oxide, lead arsenate, white arsenoid, pink arsenoid, green arsenoid, paragrene, etc.

Paris green is supposed to be copper acetoarsenite and to contain 31.29 per cent. copper oxide, 58.65 per cent. arsenious oxide, and 10.06 per cent. acetic acid.

Scheele green is supposed to be copper hydrogen-arsenite and to contain 42.37 per cent. copper oxide, 52.32 per cent. arsenious oxide, and 4.81 per cent. water.

London purple is a by-product in the manufacture of the aniline dyes and is thought to be composed mainly of calcium arsenite with some coloring impurity, mostly rosaniline arsenite.

Besides London purple there are two other preparations, Paris and English purple, which have practically the same composition.

Of course arsenious oxide should be nearly pure, but in the crude state it may contain from 8 to 10 per cent. of cinders and other impurities.

White arsenoid is supposed to be barium arsenite; pink arsenoid is supposed to be lead arsenite; and green arsenoid is supposed to be copper arsenite.

Paragrene is a patented article which is said to be free from the objectionable features of Paris green, in that it never scorches the foliage.

Excepting the arsenious oxide, all of the above preparations may be, and often are, adulterated in one of three ways:

1. Some colored substance may be used to represent the compound, which will contain none of the elements which should be in the true compound. For example, samples have been analyzed which were labeled Paris green, but which contained neither arsenious oxide nor copper. Such imitations are usually harmless to the plant, but are equally harmless to the insect. Such a fraud as the above was noticed at the Alabama Station,¹ where a sample, called Paris green, was found to be composed of Prussian blue, chrome-yellow, and some inert substance, such as clay or chalk.

¹ Bulletin No. 58.

2. Some substance or substances may be added to the insecticides to increase their weight or to change their color, for use in making pigments. For example, Paris green is often adulterated with calcium sulphate, calcium carbonate, lead chromate, etc. This second form of adulteration is practiced more often in Germany than in America.

3. There may be arsenical insecticides containing a low per cent. of arsenious oxide in combination. It will be noticed that I say in combination. Many of the insecticides contain enough arsenic to include them in the class of high-grade articles, but this arsenic is often not in combination as it should be, but present as free arsenious oxide, thus forming a substance which will scorch the foliage of the tree.

The last of these three forms of adulteration is the most common in America, and must be considered as a fraud when we remember that free arsenious oxide not only scorches the foliage, but is usually much cheaper than the compound, which ought to be present. Sometimes it appears that the free arsenious oxide is added purposely; sometimes it is free because of faulty methods of manufacture.

Paris green, or copper acetoarsenite, has been repeatedly analyzed at the New Jersey Agricultural Experiment Station,¹ and has been found to range in percentage of arsenious oxide from 41.54 to 68.59 per cent. The excessively high percentage of arsenious oxide indicates that this cheaper substance had been added to the Paris green. Again, a sample of Paris green has been recently analyzed at the California Agricultural Experiment Station,² which contained 31.25 per cent. copper oxide and 52.90 per cent. arsenious oxide, but 23.60 per cent. of arsenious oxide, or nearly one-half, was in the free state. There were, besides, small amounts of impurities, including lime, soda, silica, sulphur trioxide, zinc oxide, etc. This most likely represents a sample where faulty methods of manufacture were used.

Another sample of Paris green, analyzed at the New Hampshire Station,³ was found to have the following composition:

¹ Report, 1897, pages 397-492.

² Bulletin No. 126.

³ Bulletin No. 43.

	Per cent.
Arsenious oxide (does not say whether free or combined) ..	30.00
Insoluble in hydrochloric acid	43.30

This insoluble portion was composed mainly of silica and oxides of iron and alumina, thus indicating that clay was the adulterant used.

Again at the Massachusetts Hatch Experiment Station,¹ two samples of so-called pure Paris greens were analyzed, which, not including various small amounts of impurities, had the following compositions:

	Per cent.	Per cent.
Water at 100°	5.00	4.29
Arsenious oxide	58.44	63.98
Copper oxide	8.30	6.60
Calcium oxide	14.50	15.98
Sulphur trioxide	7.56	5.80

The above analyses, of course, show adulteration with calcium sulphate. Samples of Paris green analyzed in Germany have been found to contain calcium sulphate, barium sulphate, lead chromate, lead sulphate, calcium carbonate, etc. One especially contained 25 per cent. of barium sulphate and 6.56 per cent. of lead chromate.²

As to Scheele green, the same adulterants are found as in Paris green. In a sample which I have just analyzed, the arsenious oxide and copper oxide appear in nearly theoretical proportions, but 17 per cent. of the arsenious oxide is in the free condition, thus making the sample worthless, unless previously treated with lime.

As to London purple, a sample analyzed at the New Jersey Station showed the following composition:

	Per cent.
Water	3.27
Arsenious oxide	41.44
Calcium oxide	24.32
Alumina and iron	3.37
Sulphur trioxide	0.31
Dye by difference	27.97

The arsenic in this sample was found to be present in the form $\text{Ca}_3(\text{AsO}_3)_2$, or the normal arsenite, but about 15 per cent.

¹ Bulletin No. 38.

² Stillman: *Chem. News*, 80, Nos. 20,087 and 20,088.

was soluble; therefore, although this sample was not adulterated, the analysis shows very careless making, as the manufacturers could just as easily have boiled with enough lime in the beginning. The process of manufacture, by the way, is to boil a waste product consisting of dye and arsenious oxide with lime, to make the insoluble calcium arsenite. Samples of London purple have been analyzed at the Cornell Station,¹ South Carolina Station,² the Florida Station,³ and elsewhere, and wherever soluble arsenious oxide was determined it was found to be present in large amounts. It will also be easily seen that, owing to the intense color of London purple, various substances might be added to increase the weight without being perceptible to the naked eye.

White arsenoid, which is supposed to be barium arsenite, has recently been analyzed at the California Station⁴ and found to possess the following composition:

	Per cent.
Barium carbonate.....	44.05
Barium chloride.....	13.05
Barium oxide.....	8.18
Arsenious oxide, free.....	27.64
Lead carbonate.....	1.86
Silica.....	0.20
Water.....	4.00

It will be seen that the only substance giving to this preparation any value as an insecticide is arsenious oxide, and since this is in the free state, it is harmful to the foliage. The barium salts are present only to give weight.

Pink arsenoid is supposed to be lead arsenite. A recent analysis made at the California Agricultural Experiment Station⁴ showed that it had the following composition:

	Per cent.
Lead oxide.....	49.58
Arsenious oxide, combined.....	40.02
Arsenious oxide, free.....	3.24
Water.....	0.31
Organic matter from aniline residue and lead sulphate....	6.85

¹ Bulletin No. 18.

² S. C. Report, 1888, page 142.

³ Florida Station Bulletin No. 14.

⁴ Bulletin No. 126.

This preparation is evidently unadulterated and has given very good results.

Green arsenoid, or copper arsenite, analyzed at the California Station,¹ showed the following composition :

	Per cent.
Arsenious oxide.....	61.33
Copper oxide.....	28.83
Water.....	2.77
Silica.....	0.40
Organic material, sodium sulphate, etc.	6.67

7.82 per cent. of this arsenious oxide was soluble.

Paragrene has also recently been analyzed at the California Station and found to owe its poisonous properties mainly to arsenious acid and copper oxide. It contains 23.46 per cent. copper oxide and 40.60 per cent. of arsenious oxide, but 23.08 per cent. of this is free. It also contains 19.31 per cent. of gypsum to add weight. The preparation is therefore harmful to the plant.

In the Canada Experimental Farm Report of 1895, page 220, mention is made of lead arsenate. This substance is obtained by the action of sodium arsenate on lead acetate. It is there stated that there is no reason lead arsenate so manufactured should contain impurities, but that it often does, however, because of the original impurities in the sodium acetate, a by-product obtained in the manufacture of aniline dyes.

Arsenious oxide, because of its method of preparation, may, in the crude state, contain from 2 to 10 per cent. of arsenious sulphide and ore dust as impurities, it being usually prepared by roasting mispickel or tin ores.

I must not leave this subject without calling attention to two insecticides, called respectively "Peroxide of Silicates" and "Hammond's Slug Shot." The first, on analysis at the Vermont Station,² was shown to have the following composition :

	Per cent.
Water.....	1.44
Arsenious oxide.....	1.47
Copper oxide.....	0.28
Lime.....	36.43
Sulphur trioxide.....	52.29
Ferric oxide and aluminium oxide.....	1.40
Sand.....	1.93
Organic and volatile matter.....	4.76

¹ Bulletin No. 126.

² Bulletin No. 12.

It is needless to say that this sample, composed mostly of calcium sulphate, did not give good results.

"Hammond's Slug Shot," by an analysis made at the Vermont Experiment Station,¹ was shown to have the following composition :

	Per cent.
Water of hydration	14.76
Arsenious oxide	1.58
Cupric oxide	0.60
Lime	30.24
Sulphur trioxide	43.02
Ferric oxide and aluminum oxide	0.79
Sodium chloride	2.83
Insoluble	1.38
Organic and volatile matter (mostly dead oil by difference)	4.79

Here again it will be seen that in buying the above substance one is paying a pretty good price for an article composed almost entirely of calcium sulphate.

I have gathered together a bibliography of the arsenical insecticides, of which the examples presented above form only a small fraction. These are, however, fairly representative of the different classes of adulterants.

ANALYSIS OF INSECTICIDES.

(Paris green and Scheele green.)

Recently it became necessary for me to make analyses of various arsenical insecticides, but on looking up the matter I found that few good methods had been published. Many of the Stations had partially analyzed these substances, but even the methods employed in these partial analyses were not given. I therefore decided to test some of the few more promising methods which are known, and where methods were not known, try to work them out on the following substances: Paris green, Scheele green, London purple, and white arsenic.

An analysis of Paris green would include determinations of total and soluble arsenious oxide, copper oxide, moisture, acetic acid, and matter insoluble in dilute hydrochloric acid. An analysis of Scheele green would include determinations of all the substances named above, except acetic acid. An analysis

¹ Bulletin No. 12.

of white arsenic would, of course, include only the determinations of water and total arsenious oxide to ascertain the purity.

A determination of the moisture in Paris green is made in the usual way by drying for twelve to fifteen hours, at the temperature of boiling water. On two samples the results were :

	A. Per-cent.	B. Per-cent.
Moisture	1.30	0.99

1. For a determination of the total arsenious oxide, I first tried the well-known method, as given by Fresenius, of dissolving in hydrochloric acid, oxidizing to arsenic acid with potassium chlorate, driving off the chlorine at a gentle heat, making ammoniacal, precipitating with magnesia mixture, filtering and washing in a Gooch crucible, putting a cap on the crucible drying first at 100° and then at 130° C., heating on a sand-bath, then on an iron plate, and finally heating over the blast-lamp and weighing as magnesium pyroarsenate. This method, however, in the first place, is very long because of the time taken in getting rid of the chlorine and in igniting the precipitate by degrees; secondly, there is great danger of loss of the arsenic, as arsenious chloride; and thirdly, the precipitate of ammonium magnesium arsenate is somewhat soluble in the ammonia wash and has not quite the theoretical composition. After obtaining rather varying results, this method was abandoned.

2. I next tried to determine the arsenic by the following method: Oxidize the Paris green in a small flask, closed with a funnel on the steam-bath, by means of fuming nitric acid. Pour out in a dish and evaporate to dryness; take up with hydrochloric acid and proceed as in the first method, finally weighing the arsenic as magnesium pyroarsenate. This plan shortens the time necessary to determine the arsenic and rids one of the danger of loss as arsenious chloride, but there is still present the third source of error, mentioned above. Proceeding in this way, I obtained the following results on two samples of Paris green ("A and B"), and on a sample of dry, chemically pure arsenious oxide:¹

¹ In every case where the arsenic was weighed as magnesium pyroarsenate, a correction was made of 0.0008 gram magnesium pyroarsenate, for each 30 cc. of ammoniacal filtrate containing an excess of magnesium mixture as suggested by Fresenius.

	Arsenious oxide. Per cent.
Paris green, "A".....	{ 56.03 56.03
Paris green, "B".....	{ 56.68 56.69
Arsenious oxide, C. P	{ 99.33 99.18

3. I next tried a method suggested by Thorn Smith.¹ As described by himself, the method is as follows :

"Two grams of Paris green are weighed out and about 100 cc. of water and 2 grams of sodium hydroxide added. The solution is brought to a boil and the boiling is continued for a few minutes (thus precipitating copper as cuprous oxide). It is then allowed to cool to room temperature and the solution made to 250 cc. The well-shaken liquid is filtered through a dry filter and 50 cc. taken for analysis. This portion is concentrated to about one-half of its volume and allowed to cool to about 80°C. An equal volume of strong hydrochloric acid is then added, accompanied by 3 grams of potassium iodide, and the whole allowed to stand for ten minutes (to reduce the arsenic oxide to arsenious oxide). The deep red solution is slightly diluted with water to dissolve the precipitate caused by the potassium iodide, and a dilute solution of sodium hyposulphite added, until the color just disappears. This solution is then made neutral by the addition of dry sodium carbonate and finally an excess of sodium bicarbonate is added. Tenth normal iodine is dropped in and the end reaction noted by the starch solution."

In applying this method, I used one or two precautions, not mentioned by Smith ; namely, instead of making neutral with dry sodium carbonate and very likely getting in an excess, I added dry sodium carbonate until the bubbles came off slowly, showing that the acid was really neutralized, and then sodium bicarbonate to neutrality and some in excess. This was done, because if any free sodium carbonate is present it will itself act on the iodine solution. Again, after using up the iodine which was set free in reducing the arsenic to arsenious oxide by sodium hyposulphite, the solution was immediately diluted, since the air

¹ This Journal, 21, 769.

is apt to act on the hot, concentrated solution of hydriodic acid and set free some iodine if this is not done.¹

On applying this method to the two samples of Paris green ("A" and "B") and the dry, chemically pure arsenious oxide the following results were obtained :

	Arsenious oxide. Per cent.
Paris green "A"	{ 56.85 56.96
Paris green "B"	{ 57.63 57.45
Arsenious oxide, C. P. ²	{ 100.10 100.10 99.86

It will not be out of place here to speak of the standardization of the iodine solution, since it is upon the correctness of this standardization that the accuracy of the above method depends. A great many text-books give the following method for standardizing the iodine solution :

Weigh out a small portion of dry, chemically pure arsenious oxide, dissolve in sodium hydroxide, make slightly acid with hydrochloric acid, and then add an excess of sodium bicarbonate. Run in the iodine solution, using starch as an indicator, until the blue color appears.

I used this method of standardizing at first, but it soon seemed to me that perhaps it was not correct, since the literature on the subject speaks of the alkali arsenites being partially oxidized to the "arsenates" upon boiling the solution, exposed to the air. I therefore used a dry, chemically pure portion of arsenious oxide and carried it through by the Thorn Smith method, standardizing my iodine solution against the arsenious oxide, as finally reduced by potassium iodide. In every case, I found that on adding potassium iodide to the hydrochloric acid solution of the arsenite some iodine was set free, showing that a small amount of arsenate had been formed, which should be reduced before running in the iodine solution.

Applying these two methods to an approximately tenth-normal

¹ Gooch and Browning : *Am. J. Sci.*, 40, 66 (1890).

² The iodine solution for the determination of arsenic trioxide in the chemically pure arsenic trioxide was not standardized against arsenious oxide, but against sodium hyposulphite, which had in turn been standardized against the amount of iodine set free, when potassium iodide acts on a weighed quantity of potassium dichromate in the presence of hydrochloric acid.

iodine solution, I obtained by the old method of standardization 1 cc. iodine solution = 0.012607 gram iodine, and by the Smith method of standardization 1 cc. iodine solution = 0.012484 gram iodine. It will at once be seen that the errors caused by the sodium arsenite partially oxidizing to sodium arsenate is larger than should be allowed in a standard solution.

A determination of the copper oxide in Paris green was made in the following well-known manner:

The cuprous oxide obtained in the Thorn Smith method by boiling the Paris green with sodium hydroxide was poured on the filter (after taking an aliquot portion of the solution for the determination of arsenious oxide) and well washed with hot water. It was then dissolved with hot dilute nitric acid and made to a volume of 250 cc., one-fifth being taken for analysis. The copper in solution was determined either by means of the galvanic current or, when that was not handy, in the following manner:

The nitric acid solution was made alkaline with sodium carbonate, then made slightly acid with acetic acid, and about ten times the weight of the copper in potassium iodide added. When it was all dissolved, the free iodine was titrated with a standard solution of sodium hyposulphite, using starch as indicator. The full details of this method are given in Sutton's "Volumetric Analysis," third edition, page 133. The results on the two samples of Paris green by this method were as follows:

	Cupric oxide. Per cent.
Paris green "A".....	{ 29.79 30.37 30.15
Paris green "B"	{ 29.79 29.79 29.79

The figure for acetic acid in Paris green is usually obtained by subtracting the sum of total arsenious oxide, water, cupric oxide, and residue left after treating with dilute hydrochloric acid, from 100.

As to the determination of soluble arsenic in Paris green, I could find very little in the literature on the subject which was of any value. I therefore tried several schemes:

1. I weighed 1 gram of Paris green on a filter-paper and washed it with cold water. Each time 200 cc. were obtained, sodium bicarbonate was added and the solution titrated with iodine solution. After about 2,000 cc. of wash liquor had been used the filtrate was still slowly gaining in arsenious oxide. The method was therefore abandoned as impracticable.

2. I weighed out several 1-gram samples of Paris green and treated these in flasks with 500 cc. of water. The flasks were stoppered and occasionally shaken each day. Every few days an aliquot portion of 100 cc. was filtered off from one of the flasks and the arsenious oxide titrated with iodine after the addition of sodium bicarbonate. The results on the samples of Paris green ("A" and "B") were as follows:

	Time. Days.	Arsenious oxide extracted. Per cent.
Paris green "A".....	2	1.01
" " "	4	1.68
" " "	8	2.69
" " "	11	4.02
" " "	14	4.02
" " "B"	9	3.41
" " "	12	4.86
" " "	14	4.86

It will thus be seen that this method finally gave constant and very likely correct results. It is rather long, but very little attention or time had to be given after the first weighing out.

3. To expedite matters, I next tried the following method for determining the soluble arsenious oxide. One-half gram of Paris green was weighed out, placed in a flask and treated with about 200 cc. of water. This was digested with occasional shaking on the water-bath at 50° to 60° C., and each day all of the water poured off through a filter, and, after returning all of the substance from the filter to the flask, a fresh portion of water was added and the digestion continued. The arsenious oxide was determined by means of a standard iodine solution. The results on the samples of Paris green ("A" and "B") were as follows:

	Time. Days.	Arsenious oxide extracted. Per cent.
Paris green "A".....	1	3.41
" " ".....	2	$3.41 + 2.14 = 5.55$
" " ".....	3	$5.55 + 1.56 = 7.11$
" " ".....	4	$7.11 + 1.17 = 8.28$
" " ".....	5	$8.28 + 1.26 = 9.54$
" " ".....	6	$9.54 + 1.56 = 11.10$
" " ".....	7	Still gaining.
" " "B".....	1	2.24
" " ".....	2	$2.24 + 1.46 = 3.70$
" " ".....	3	$3.70 + 1.26 = 4.96$
" " ".....	4	$4.96 + 1.17 = 6.13$
" " ".....	5	$6.13 + 1.17 = 7.30$
" " ".....	6	$7.30 + 1.56 = 8.86$
" " ".....	7	Still gaining.

It will thus be seen that a hot extraction can not be used, since the Paris green either breaks up or goes into solution in the presence of hot water, the amount of arsenious oxide going into solution each day being finally nearly constant.

The same methods for determining the constituents of Scheele green were used as those for Paris green mentioned above. On one sample the moisture was 5.27 per cent.

The total arsenious oxide was as follows:

By Method 1. Oxidation with HCl and KClO ₃	Not tried
By Method 2. Oxidation with HNO ₃	$\left\{ \begin{array}{l} 50.63 \\ 50.80 \end{array} \right.$
By Method 3. Thorn Smith.....	$\left\{ \begin{array}{l} 51.39 \\ 51.27 \end{array} \right.$

The determination of the cupric oxide by the method mentioned above gave the following results:

Cupric oxide.....	$\left\{ \begin{array}{l} 38.04 \\ 38.23 \end{array} \right.$
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The soluble arsenious oxide determination gave the following results by the various methods:

1. Washing on filter. Not tried.
2. Extracting with 500 cc. cold water:

Time. Days.	Arsenious oxide extracted. Per cent.
6.....	13.09
9.....	14.30
13.....	16.26
21.....	16.73
34.....	17.82
36.....	17.70

3. Extracting with water at 50° to 60° C.:

Time. Days.	Arsenious oxide extracted. Per cent.
1	13.43
2	$13.43 + 3.70 = 17.13$
3	$17.13 + 1.85 = 18.98$
4	$18.98 + 0.87 = 19.85$
5	$19.85 + 0.78 = 20.63$
6	$20.63 + 0.58 = 21.21$
7	$21.21 + 0.49 = 21.70$
8	$21.70 + 0.39 = 22.09$
9	$22.09 + 0.39 = 22.48$
10	$22.48 + 0.39 = 22.87$
11	Still gaining.

From the above work I would draw the following conclusions:

1. Water can be determined in Paris green and Scheele green by drying at the temperature of boiling water for twelve to fifteen hours.

2. The best method for determining the total arsenious oxide in Paris and Scheele greens is the Thorn Smith method, marked 3 above.

3. The best method for determining the soluble arsenious oxide in Paris and Scheele greens is by extracting with 500 cc. of water at room temperature.

4. Hot water extraction can not be used to extract soluble arsenious oxide.

5. A good method for determining copper in Paris and Scheele greens is the volumetric method based on the titration of the iodine set free from potassium iodide by a copper salt in acetic acid solution.

Appended is a condensed statement of the work done:

	Water. Per cent.	Total arsenic.		
		Oxidation with potas- sium chlorate.	Oxidation with nitric acid.	Method of Smith.
			Per cent.	Per cent.
Paris green "A".....	1.30	Abandoned	56.03	56.90
Paris green "B".....	0.99	"	56.69	57.54
Scheele green	5.27	"	50.66	51.33
Arsenious oxide, C. P.	None	"	99.25	100.02

	Soluble arsenious oxide.				
	Wash on filter.	500 cc. cold water. Per cent.	Water at 50°-60° C.	Cupric oxide. Per cent.	Insoluble in hydrochloric acid.
Paris green "A".....	Abandoned	4.02	11.10+	30.07	None
Paris green "B".....	"	4.86	8.86+	29.79	None
Scheele green.....	"	17.76	22.87+	38.14	None
Arsenious oxide, C. P.	None

A continuation of this paper will appear during the next few months, which will have for its object the creation and improvement of the methods of estimating the various constituents of London purple as well as a study of the improved method of estimating arsenic gravimetrically by Martha Austin,¹ which has only come to my notice since the above work was completed.

THE DETECTION OF COAL-TAR DYES IN FRUIT PRODUCTS.

By A. L. WINTON.

Received July 5, 1900.

SOON after its discovery fuchsine came into use for coloring wines and replaced to a large extent the vegetable dyes which from very early times had been employed for this purpose. More recently various other coal-tar dyes, particularly the azo-colors, have been extensively used in wines although fuchsine and acid fuchsine are still preferred by some makers.

Within the past few years the use of coal-tar dyes in articles of diet has attracted the attention of food analysts in the United States. In the case of confectionery, pastries, and some other products they serve merely to render the articles more attractive to the eye without deceiving the purchaser, but as a rule they give imitation products the appearance of the genuine or, to use the legal phraseology, "they make the products appear better or of greater value than they really are."

Some of the results obtained by Winton, Ogden, and Mitchell, in the examination of foods at the Connecticut Agricultural Experiment Station, illustrate the fraudulent use of dyes. In 1898, sixty-three samples of jellies purporting to have been made from fruit were examined, and of these, twenty-eight were spurious mixtures colored with coal-tar dyes. Some of the most remarkable samples, labeled "strawberry jelly," "raspberry

¹ *Ztschr. anal. Chem.*, 23, heft 2.

jelly," etc., consisted of starch paste, flavored with artificial "fruit ethers," sweetened with glucose and preserved with salicylic acid, the dye having been used to carry out the deception. Of twenty-eight samples of fruit preserves, eight were also colored with coal-tar dyes. During the following year (1899) ninety-two samples of soda-water sirups, chiefly strawberry, raspberry, and orange, were subjected to analysis. Of these, forty-five were colored with coal-tar dyes. As a rule the sirups which were artificially colored were also artificially flavored and contained no genuine fruit juice whatever. Dyes were also found in bottled carbonated beverages.

The relation of these dyes to public health deserves attention. The experiments carried on with dogs and other animals by Cazeneuve and Lépine, Weyl, and others have proved beyond a doubt the poisonous nature of picric acid, dinitrocresol, and Martius' yellow, among the nitro-colors, and of orange II and metanil yellow among the azo-colors. Fuchsine, sulphonated nitro-colors, and most of the azo-colors did not act as poisons although some of the azo-colors produced vomiting, others diarrhea, and many developed slight albuminuria.¹

Although there is evidence that the bulk of the coal-tar dyes are not injurious to some of the lower animals, it is not safe to assume that they are entirely harmless to human beings. The dog, the animal used in most of Weyl's experiments, has a proverbially strong stomach and eats, with no apparent discomfort, many things which would disturb the digestion of a man.

The unwholesomeness of certain coal-tar dyes not classed as poisons is indicated by the experience of Weber² who tested their effect on the artificial digestion of fibrin with pepsin and with pancreatin. He found that oroline yellow (acid yellow) retarded the action of pepsin and that methyl orange, saffoline (acridine red), and magenta (fuchsine) seriously interfered with the pancreatic digestion. Of these, fuchsine, at least when pure, had been pronounced entirely harmless by earlier investigators who based their conclusions on experiments with lower animals and some few with man.

¹ "The Coal-tar Colors" by Theodore Weyl, translated by Henry Leffmann, pp. 54-148.

² This Journal, 18, 1092.

Even if the entire harmlessness of most of the coal-tar dyes is conceded, in view of the injurious properties of some of them and the difficulty of distinguishing these from the harmless dyes when present in food products, the safe course is to exclude all dyes of coal-tar origin from articles of diet. In Austria their use is entirely prohibited and in other countries they are regarded with suspicion.

In carrying out the work of food examination under adulteration laws the analyst is often called upon to determine whether or not a coal-tar dye is present, if not to identify the particular dye.

Numerous methods of testing wines for these dyes are described in the journals and in the works on food analysis but almost nothing has been published on their detection in jellies, preserves, fruit sirups, and other fruit products.

Because of the absence of special methods I have adapted some methods originally devised for wines for use in testing other products and publish the following details, with precautions learned by experience, for the benefit of others engaged in similar work.

In applying these tests to jellies and other semisolid products it is necessary to bring into solution by boiling with 1 to 5 parts of water.

ARATA'S WOOL TEST.¹

One hundred cc. of the liquid to be tested, prepared if necessary as described in the preceding paragraph, are boiled for ten minutes with 10 cc. of 10 per cent. solution of potassium bisulphate and a piece of white wool, or woolen cloth, which has been previously heated to boiling in a very dilute solution of sodium hydroxide and thoroughly washed in water. After removal from the solution, the wool is again washed in boiling water and dried between pieces of filter-paper. If the coloring-matters are entirely from fruit, the wool either remains uncolored, or takes on a faint pink or a brown color which is changed to green by ammonia and is not restored by washing in water; but if certain coal-tar dyes, chiefly of the azo-group, are present,

¹ *Ztschr. anal. Chem.* 28, 639. See also Borgman: "Anleitung chem. Anal. d. Weines," Wiesbaden, 1898, p. 91. Koenig: "Untersuchung landw. u. gewerb. wich. Stoffe," Berlin, 1898, 577.

the wool is dyed and the color on the fibers is either not changed by ammonia or, if changed, is restored by washing.

The dye present may often be identified by noting the color of the wool after addition of enough concentrated sulphuric acid to thoroughly moisten the fibers and again after dilution of the acid.¹ As a rule it is not desirable to proceed further with the test although Arata gives instructions for removing the dye from the wool and testing the dye itself. For this purpose the wool is treated with dilute tartaric acid solution to remove vegetable colors, washed in water and dried between sheets of filter-paper. It is then transferred to a test-tube and saturated with concentrated sulphuric acid. After standing five or ten minutes, water sufficient to make 10 cc. is added and the wool is removed. The solution after making alkaline with ammonia and cooling is shaken with 5 to 10 cc. of pure amyl alcohol, to which a few drops of ethyl alcohol are added, to facilitate the separation. The alcoholic extract is separated, evaporated to dryness, and the residue tested according to the scheme of Girard and Dupré, Witt,² Weingaertner³ or Dommergue.⁴

I have applied this test to samples of juices, sirups, jellies, and preserves prepared in the laboratory from the fruits, as well as to numerous commercial fruit products including catsups. The woolen cloth used was "nun's veiling" cut into pieces one inch wide and three inches long.

When strawberry, raspberry, blackberry, currant, grape, and cherry juices, without dilution, were treated as has been described, the wool acquired a dull pink or brownish pink color. With ammonia the color changed to green, and washing with water in no case restored the original color. Treatment with 10 per cent. tartaric acid solution in the cold was without effect, but on boiling for some time the pink color was largely removed. From orange, lemon, pineapple and tomato juice or pulp, the wool absorbed no color at all, or only a faint yellow color.

Jellies, preserves, sirups, and catsups known to be pure gave up to the wool very slight colors, but many of the commercial

¹ See scheme of Girard et Dupré: "Analyse des Matières Alimentaires et Recherche de leurs Falsifications."

² *Ztschr. anal. Chem.*, 26, 100.

³ *Ibid.*, 27, 232.

⁴ *Ibid.*, 29, 369.

products imparted to the wool intense red, orange, magenta, and even green shades. Treated with ammonia, these bright colors remained unchanged or, if changed, washing restored the original color.

Boiling with tartaric acid solution also failed to affect the colors. By treatment with concentrated sulphuric acid and dilution of the acid, color reactions for acid fuchsine, tropæolins, ponceaus, Bordeaux red, eosins, and other dyes were obtained.

I have found it more satisfactory to test the dyed wool directly, rather than the color obtained from the wool as directed by Arata, because only a few dyes are extracted by amyl alcohol from alkaline solutions, and, as explained further on, tests of the residues left after evaporating the extracts are indecisive.

Care should be taken to determine whether the wool is dyed, or merely coated with the color. For example, chlorophyl from green coloring preparations of vegetable origin, is deposited on wool, together with fat and resin, but the color, unlike the coal-tar dyes, rubs off on the fingers and is readily washed out with soap and water.

For the purpose of illustrating the amount of artificial color present in each glass of adulterated carbonated beverages, I have employed 250 cc. portions of the beverages (or 40 to 50 cc. of sirups diluted to 250 cc.) and pieces of nun's veiling six inches square. The dyed squares thus obtained furnish striking object lessons. From strawberry, raspberry, cherry, and blood-orange flavors, brilliant red and magenta shades were fixed on the wool (acid magenta, Bordeaux red, ponceaus, etc.); from orange and lemon flavors, orange and yellow shades (tropæolins, etc.); and from mint preparations, bright green and yellow-green colors.

AMYL ALCOHOL TEST, ALKALINE SOLUTION.¹

Twenty-five cc. of the liquid to be tested, made alkaline with ammonia, are shaken cautiously for some minutes in a separatory funnel, with pure amyl alcohol. If the clear alcoholic layer, when separated from the aqueous solution, is colored, or if addition of acetic acid develops a magenta color (fuchsine), a portion of it, together with an equal bulk of water and a thread of

¹ "Analyse des Matières Alimentaires et Recherche de leur Falsifications", Par Girard et Dupré, pp. 167, 582.

wool, is heated on a water-bath, the water lost by evaporation being replaced from time to time.

The presence of a coal-tar dye should not be affirmed until the color has been fixed on wool and the wool has been washed in boiling water, dried, and tested with sulphuric acid. When fuchsine is present, the color which appears on adding acetic acid to the alcohol extract is changed to yellow by hydrochloric acid. Ether or ethyl acetate may be used in place of amyl alcohol for extracting fuchsine.

AMYL ALCOHOL TEST, ACID SOLUTION.¹

Twenty-five cc. of the liquid, to which have been added a few drops of hydrochloric acid, are shaken with amyl alcohol, and dyeing tests are made as described in the preceding section.

A colored amyl alcohol does not prove the presence of a coal-tar color, as I have found that red coloring-matters are extracted by this solvent from acid solutions of pure fruit juices. These solutions, however, do not dye wool, when treated as above described.

Some authors recommend that the sulphuric acid test be applied to the residue left after evaporating the amyl alcohol extract. This may be satisfactory in wine analysis but with fruit jellies, etc., this residue is liable to contain other organic matters which obscure the color reactions of coal-tar dyes.

If amyl alcohol extracts from the liquid, after acidifying, an orange color which has not been found to be of coal-tar origin, test may be made for cochineal.

The alcohol is washed several times with water and divided into two portions. To one portion is added a solution of uranium acetate, drop by drop, with shaking. In the presence of cochineal the aqueous solution acquires an emerald-green color.² As a confirmatory test the other portion is made alkaline with ammonia which changes the orange color of cochineal to purple.

GIRARD'S TEST FOR ACID FUCHSINE (ACID MAGENTA).³

If a bright magenta color is fixed on wool by Arata's test and

¹ "Analyse des Matières Alimentaires et Recherche de leur Falsifications," Par Girard et Dupré, p. 582.

² *Ibid.*, p. 580.

³ *Ibid.*, p. 169.

if ordinary fuchsine has been proved to be absent, test should be made for acid fuchsine.

To 10 cc. of the liquid are added 2 cc. or more of 5 per cent. solution of potassium hydroxide. The strongly alkaline liquid is mixed with 4 cc. of 10 per cent. solution of mercuric acetate and filtered. The filtrate should be alkaline and colorless. If addition of a slight excess of dilute sulphuric acid produces a violet-red coloration and other dyes have not been found by the amyl alcohol test, the presence of acid fuchsine may be affirmed.

I have found this test useful in the examination of fruit juices and sirups but unsatisfactory in the case of jellies owing to difficulties in filtration and undecisive reactions.

CAZENEUVE'S METHOD.

Cazeneuve's mercuric oxide method¹ for detection of coal-tar dyes which has been extensively employed in wine analysis did not prove satisfactory in the examination of jellies. This method, however, deserves trial with fruit juices and sirups, which are more easily handled than the gelatinous products.

In testing a suspected sample I apply first of all Arata's test. The other tests described are employed either to confirm the results obtained by Arata's test or to supply evidence in cases where that test fails.

The analyst should be extremely cautious in naming the particular dye present in a sample. It should be remembered that the number of coal-tar dyes on the market is exceedingly large and that new dyes are continually being introduced. A reaction which a few years ago may have been characteristic of a particular dye may to-day be common to several dyes. As a rule it is only necessary to learn whether or not a color is of coal-tar origin. In fact such terms as "red coal-tar dye" and "orange coal-tar dye" are often to be preferred in an official report to the cumbersome scientific names or the equally unintelligible commercial names.

CONNECTICUT AGRICULTURAL EXPERIMENT STATION,
NEW HAVEN, CONN., June, 1900.

¹ "Analyse des Matières Alimentaires et Recherche der leur Falsifications," Par Girard et Dupré, p. 174; *Compt. rend.*, 102, 52.

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION
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ESTIMATION OF FAT IN CONDENSED MILK.

BY ALBERT E. LEACH.

Received July 9, 1900.

THE use of canned, sugar-preserved, condensed milk has increased considerably during the last few years, no less than forty brands of the article being on sale in Massachusetts at the present time. In view of the fact that of all its ingredients the fat is the only one that can be conveniently tampered with to produce an inferior or cheaper product, it becomes highly important to have at hand a ready and accurate means of fat determination, especially where samples have to be examined systematically and in large numbers for adulteration.

The Babcock centrifuge method, so convenient for estimating fat in ordinary milk, was long thought to be out of the question for use with sugar-preserved milk, by reason of the fact that the cane-sugar, which is present to the extent of some 40 per cent. in the average condensed milk, becomes so charred by the action of the sulphuric acid employed in the test as to produce nothing but a black mass in place of the desired column of clear fat. This has been the common experience of all who tried it.

The Adams-Soxhlet method, which is the recognized standard for fat determination in ordinary milk, has been largely used in the case of condensed milk, -but, in the writer's experience, can not be depended on for the latter purpose, on account of the fact that the large amount of cane-sugar present, even when the sample is diluted for analysis, encloses the fat particles so firmly, when dried on the extraction coil, as to render its removal by the solvent ether a very difficult matter.

In 1895 the writer devised a scheme whereby the Babcock machine could be satisfactorily used for condensed milk fat, and an outline of the process as then carried out was published in the "Annual Report of the Massachusetts State Board of Health for 1896." This process, with certain minor modifications which experience has from time to time suggested, has been in successful use in the Food and Drug Department of the Board for over five years, and has proved itself to be not only much quicker

than the Adams-Soxhlet extraction method and easier of manipulation, but, indeed, more accurate, by reason of the fact that the cane-sugar with all its attendant troubles is first eliminated.

If, in the case of condensed milk, ordinary ether is used as a reagent for the Soxhlet extraction, the amount of extract weighed as fat may not *appear* too low, because the alcohol and water present in the ether dissolve not only fat, but also sugar, which goes in with, and is weighed as fat. On the contrary, if the ether be dehydrated with calcium chloride and distilled over sodium, to free it completely from alcohol, the extracted fat will be found to be far too small. The same incomplete extraction results from the use of benzine or petroleum ether as a solvent.

Parallel determinations of fat in sugar-preserved milk by the Adams-Soxhlet process, using ether carefully dehydrated and freed from alcohol, and by the writer's method involving the use of the Babcock machine, show in all cases a larger fat content by the latter or modified Babcock process. Indeed, in one instance an extraction of sixty hours was required in the case of the Soxhlet process to equal the percentage of fat found by the modified Babcock process, so firmly were the fat particles enclosed by the cane-sugar on the extraction coil, thus resisting the action of the ether. It is obvious that, in the case of the modified Babcock process, no more fat can be shown by the final result than actually exists in the milk; indeed, if anything, one would expect a slight loss, so that, when compared with the Soxhlet method, if the latter shows lower figures, it can safely be presumed that the process is unreliable. This, of course, applies only to the sugar-preserved variety of condensed milk.

The improved method of fat estimation with the Babcock centrifuge is as follows: Having first insured a homogeneous sample of the contents of the can by stirring, 40 grams are weighed out preferably in a weighing tray for sugar, transferred by washing to a graduated 100 cc. sugar flask, and made up to the mark with water. Twenty-five cc. of the thoroughly mixed diluted sample, corresponding to 10 grams of the original condensed milk, are measured by a pipette into an ordinary test-bottle of the Babcock centrifuge. This is filled nearly to the neck with water, and 4 cc. of a solution of copper sulphate of the strength of Fehling's copper solution are added. The contents are thor-

oughly shaken, and the precipitated proteids, carrying with them the fat, are rapidly separated out by whirling the fat bottle in the centrifuge, preferably (though not necessarily) without heating. The writer prefers an electric centrifuge of the Robinson type for this purpose, as the heat of the steam-driven machine cakes the precipitate down, so that it is harder to wash. If desired, the precipitate may be allowed to settle out of itself, which it does more quickly in the cold.

The supernatant liquid containing the sugar is drawn off by means of a pipette of large capacity, having a stem sufficiently small to pass easily into the neck of the milk bottle, a small wisp of absorbent cotton being first twisted over the bottom of the pipette to serve as a filter. If many samples are to be treated, a suction-pump, connected by rubber tubing with the pipette, is a great convenience. On withdrawing the pipette with the sugar solution, the cotton is wiped off into the bottle by rubbing against the inner side.

The precipitated proteids and fat are given two additional washings, as above, by shaking thoroughly with water introduced nearly to the neck of the bottle, separating out in each case by centrifuge or by settling, and finally removing the washings with the pipette, two of such extra washings being found nearly always sufficient to remove all the sugar. If the precipitate is caked down hard after treatment with the centrifuge, it may be necessary to employ a stiff platinum wire as a stirrer to aid in mixing with the wash-water.

Finally, enough water is added to amount approximately to the normal volume of 17.6 cc. usually employed for the Babcock test, 17.5 cc. of sulphuric acid are added, and the test continued from this point on as in the ordinary Babcock process of milk testing, multiplying the reading obtained by 1.8 to give the correct percentage of fat in the sample.

For condensed milk containing no added cane-sugar, these precautions are, of course, unnecessary, the ordinary Babcock method being directly employed with a weighed portion of the milk.

ON CERTAIN PECULIARITIES IN THE URINE OF VEGETARIANS.

By J. H. LONG.

Received July 23, 1900.

I HAVE recently presented the results of analyses of a number of normal urines¹ in which the relation of the copper oxide reducing power to the amounts of creatinin and uric acid present, was especially noted. In this paper I shall give briefly the corresponding data found by examining the urine of individuals living wholly on a vegetable diet. As the methods of examination were the same as formerly employed, it will not be necessary to refer to them again. The seven men who furnished the urine for the tests are students of the American Medical Missionary College of Battle Creek and Chicago, and for a year or longer had lived on a diet of bread, fruits, vegetables, and prepared cereal and nut foods exclusively. Eggs were not eaten, and only as much milk as was taken with the "cereal coffee" used. The whole day's excretion was furnished me in each case. The table following gives the important data secured as explained in the heading over each column.

No. of sample.	Excretion in twenty- cc. four hours.	Specific gravity at 20°	Urine required to re- duce 50 cc. of copper solution.	Ammonia from 1000 cc. of urine. Mg.	Urea from 1000 cc. of urine by Liebig pro- cess. Gms.	Uric acid from 1000 cc. of urine. Mg.	Creatinin from 1000 cc. of urine. Mg.	Chlorine from 1000 cc. of urine. Gms.	P.O. ₅ from 1000 cc. of urine. Gms.
1	800	1.029	16.2	745.0	28.9	668.5	1551.6	6.65	1.89
2	805	1.030	16.3	522.0	28.8	645.0	1288.7	9.66	1.77
3	850	1.030	18.1	431.7	30.6	693.7	556.0	8.44	2.07
4	610	1.031	18.2	607.3	28.5	622.5	87.4	9.15	2.09
5	975	1.032	17.3	944.2	40.7	930.0	958.8	6.60	2.41
6	920	1.031	18.5	854.1	34.7	817.5	1123.7	7.88	2.38
7	494	1.030	16.7	507.7	32.4	765.0	362.8	6.10	1.40
8	1040	1.023	25.7	483.9	27.5	626.2	170.7	6.24	1.81
9	685	1.032	16.5	896.8	36.6	753.7	795.9	6.17	2.40
10	1025	1.029	19.6	982.2	33.8	588.7	847.6	5.75	2.50
11	1065	1.029	21.1	640.5	29.2	746.2	1337.3
12	850	1.030	19.1	716.5	31.9	810.0	1157.8

This Journal, 22, 309.

No. of sample.	Excretion in twenty-cc. four hours.	Specific gravity at 20°.	Urine required to reduce 50 cc. of copper solution.	Ammonia from 1000 cc. of urine.	Urea from 1000 cc. of urine by Liebig process.	Uric acid from 1000 cc. of urine.	Creatinin from 1000 cc. of urine.	Chlorine from 1000 cc. of urine.	P ₂ O ₅ from 1000 cc. of urine.
13	800	1.031	17.1	626.3	34.8	843.7	790.1
14	1020	1.028	19.2	498.2	28.8	705.0	889.6
15	850	1.030	20.2	711.7	32.2	952.5	1082.7	9.77
16	800	1.030	17.9	1043.9	38.8	731.2	1137.2
17	950	1.027	22.8	616.8	28.6	656.2	1017.4	8.17
18	1020	1.027	22.7	607.3	26.8	645.0	1003.0	10.19
19	800	1.031	16.1	683.2	33.2	1166.2	1558.8	7.68
20	950	1.031	19.2	1062.8	35.8	843.7	805.7	9.02
21	925	1.030	17.3	1262.1	37.1	978.7	1157.8	9.06
22	905	1.030	18.4	1072.3	34.2	746.2	1547.0	9.38
23	860	1.030	17.2	920.5	41.6	780.0	361.1
24	970	1.028	21.6	664.3	32.4	705.0	247.5	8.35	1.85
Mean	874	1.030	18.9	754.2	32.8	767.6	909.8	8.01	2.05

At first sight we notice the rather marked reducing powers of these urines which in the mean appears to be about 20 per cent. greater than in the cases described before. But at the same time it will be observed that these urines in general are highly concentrated, the average daily excretion being only 874 cc. as against 1167 cc. for the former series. If weakened then to the same dilution the total copper oxide reducing power, expressed in these terms, would be brought down even lower. In other words, for the daily excretion the reduction is not large. The probable reason for this will be evident from what follows.

Making due allowance for differences in concentration there is nothing noteworthy in the excretion of urea, uric acid, and ammonia, or for chlorine and phosphoric acid found in part of the cases, but for the excretion of creatinin we have remarkably low figures in general. The former investigation gave as the normal relation of uric acid to creatinin about 1 : 2, but here we have about 1 : 1.2. The value for the uric acid excretion is based on a volume of 1000 cc. but if calculated for the volume voided in twenty-four hours, is brought down to 671 milligrams, which is a fair average.

The correspondingly low creatinin points apparently to low metabolism, and is a fact of considerable importance. Creatinin is supposed to reach the urine in one of two ways. Many physiologists (for illustration see Schaefer's "Text-book of Physiology," p. 599) attribute it mainly or wholly to the creatin found in the lean meat consumed as food, and changed by dehydration in the liver, while on the other hand, it may be a product of body muscle metabolism. That it is not necessarily dependent on the creatin of meat has long been recognized by numerous writers since its appearance in urine during starvation has been abundantly demonstrated. The above tests fully confirm this view. The food of the persons furnishing the urines for experiment was certainly free from anything more than traces possibly of either creatin or creatinin, and had been for a period of months or years. Yet we find a creatinin excretion which is within the limits given as normal in many of our text-books. This must be traced to muscular creatin, formed in turn by metabolism of the food proteids. This view is rendered more probable by the discovery pointed out by several recent writers of the close relation of creatin and similar bodies to the derivatives of proteids formed by various hydrolytic cleavages. Although the simple relation suggested by Drechsel¹ in which the resemblance of creatin to lysatin was shown, no longer appears to hold since Hedin and others have made it evident that lysatin is probably a mixture of arginin and lysin,² we still have the creatin-like nature of arginin itself as a very interesting fact³ pointing to the same general relation. The fact that the hexone bases are produced in trypsin digestion as well as by acid hydrolysis⁴ has probably no bearing in the case in suggesting another possible source of the creatinin found, besides that of muscle katabolism, as the amounts which may be so formed are usually very small.

That the creatinin was relatively low in all the urines was probably due to low food consumption and metabolism. The men furnishing the urine performed little muscular work and took but little exercise. In a few cases the results were very

¹ *Ber. d. chem. Ges.*, 23, 3096.

² *Ztschr. physiol. Chem.*, 21, 297.

³ Schulze and Winterstein : *Ztschr. physiol. Chem.*, 26, 1.

⁴ See papers by Kossel and Mathews and by Kutscher : *Ztschr. physiol. Chem.*, 25, 199 and 195, in illustration.

low; this can not be explained by accidental error in the experimental methods, concentration of the urine with alkaline reaction, for example, but must depend on some relation not present discernible. The tests were all carefully made in the same manner and precautions were taken to secure a final concentrated filtrate in which zinc chloride would certainly precipitate any creatinin present.

The distribution of the reducing power in these urines is also interesting. It will not be necessary to make the calculation for each case as was done in the former paper, but the average results may be taken. The table above gives 18.9 cc. of urine in the mean as the volume required to reduce 50 cc. of the standard copper solution containing 2.604 grams of cupric oxide per liter. From this it may be calculated that 1000 cc. of the urine would reduce 6.888 grams of cupric oxide. This is a high figure because of the marked concentration of most of the urine. Making a similar calculation from the data of the last paper we find that the creatinin of 1000 cc. of the average urine would reduce 1.282 grams of cupric oxide, while the uric acid would reduce 1.091 grams. The sum of these reductions is 2.373 gram or a trifle over one-third of the total reduction. We have remaining 4.515 grams of cupric oxide per liter as the amount corresponding to the carbohydrates or similar bodies present. In view of the character of the food consumed this is an interesting but not unexpected result. Allowing for the concentration the reduction due to carbohydrates is still large. It is evident, therefore, that a diet wholly vegetable, in which carbohydrates and fats predominate, favors the increase in the non-nitrogenous (probably carbohydrate) factors in the urine. My thanks are due to Mr. Frank Wright and Mr. Charles Erickson for the experimental work.

NORTHWESTERN UNIVERSITY, CHICAGO,
June 20, 1900.

REVIEWS.

AN EXPERIMENTAL STUDY OF RADIO-ACTIVE SUBSTANCES.¹

Professor Röntgen's remarkable discovery, in 1895, of the penetrating rays called by him X-rays, but now equally well known by his own name, was followed in 1896 by Becquerel's announcement that the salts of uranium emit invisible radiations capable of discharging electrified bodies and of producing skiagraphic images on sensitive plates. He found that potassio-uranic sulphate emits rays that pass through black paper and affect photographic plates; this property is not limited to the brilliantly fluorescent uranic salts, but is shared by the non-fluorescent uranous salts. All uranium compounds examined proved to be active, whether phosphorescent or not, whether crystalline, melted or in solution; and metallic uranium exhibits the phenomena in a marked degree. The permanence of this property is amazing, substances kept in a double leaden box more than three years emitted rays having almost as much power as when first tested.

Shortly after the announcement by Becquerel, experimenters found that other substances have the power of emitting these "Becquerel rays;" M. Henry found it in phosphorescent zinc sulphide, Niewenglowski in insolated calcium sulphide, Troost in artificial hexagonal blende, and Schmidt in thorium compounds. In 1898 Mme. Sklodowska Curie, working in the laboratory of the Municipal School of Industrial Physics and Chemistry in Paris, devised a special apparatus for measuring the electrical conductivity of the air when under the influence of "radio-active bodies," and by its means studied the behavior of the minerals pitchblende, chalcocite, autunite, cleveite, monazite, orangeite, and thorite, and found them all active. Some varieties of pitchblende showed more than three times as much energy as metallic uranium itself, and this led her to the conclusion that the peculiar property was due to some unknown body contained in the mineral, and not to uranium compounds. Associating with her, her husband, Mme. and M. Curie attacked the mineral pitchblende with acids and reagents and soon obtained results that were presented by M. Becquerel to the Academy of Sciences, Paris, at a meeting held Monday, 18th July, 1898.

These savants showed that pitchblende contains a substance, apparently analogous to bismuth, which emits Becquerel rays

¹ Read at a meeting of the Chemical Society of Washington, held April 27, 1900, at Baltimore, Md.

4000 times stronger than uranium; they were unable to isolate the element having radiant power but they named it "Polonium," in honor of the native land of Mme. Curie. In December of the same year the lady received the Gegner prize of 4000 francs awarded her by the Academy of Sciences, and later in the same month M. and Mme. Curie, together with M. Bémont (director of the Municipal Laboratory), announced the discovery of a second radio-active body in pitchblende, which they called "Radium." Since that date Mme. Curie and her husband have industriously carried on investigations, publishing their results in the *Comptes rendus*; and some German physicists, not gallant enough to leave the enterprising woman a clear field, have announced some minor discoveries. From these papers we gather the following facts concerning these marvelous bodies.

As yet, comparatively little is known of the chemistry of the salts of polonium, since the radio-active substance has not been separated from its companions; on working up the mineral pitchblende the polonium is found in the precipitate thrown down by hydrogen sulphide, and insoluble in ammonium sulphide. Solutions of polonium react like those of bismuth, being precipitated by water.

The mixture of substances in which radium shows its activity has been more fully studied; the yet unknown element accompanies barium in analytical separations, its chloride is wholly soluble in water, and it responds to the usual tests for barium. The spectrum of the substance shows the bands of barium together with other lines peculiar to radium.¹ Attempts to separate radium from barium have been unsuccessful, but by fractional precipitation of the mixed chlorides with alcohol a salt has been obtained having 900 times the activity of uranium.

By operating on half a ton of the residues of uranium minerals Mme. Curie obtained 2 kilograms of material rich in radium. With this, attempts were made to determine the atomic weight of radium, and she found the figures 140, the atomic weight of barium being 136.4.

The extraordinary physical properties of the rays emitted by these bodies have commanded the most attention; they possess luminosity, actinic and skiagraphic power, and render the air through which they pass a conductor of electricity. This latter property, the one which led to their discovery, is studied by means of an electroscope of special construction. It consists essentially of a gold-leaf (or aluminium foil) electroscope enclosed in a metallic box with glass sides and communicating with a metal disk exterior to the box. This disk lies in a horizontal plane a few centimeters above another parallel disk which serves as a support for the substances under examination.

¹ Demarcay: *Compt. rend.*, 129, 716, Nov. 6, 1899.

When the electroscope is charged by rubbing the upper disk with a piece of ebonite, the gold-leaf diverges from the perpendicular and will remain so for some time if undisturbed; on placing a layer of any radio-active body on the insulated lower disk the air between the two disks becomes a conductor and the gold-leaf at once resumes its normal position. To estimate the rapidity of the displacement of the gold-leaf, a microscope fitted with a micrometer eye-piece is attached to the apparatus at right angles to the axis, and with the aid of a watch beating seconds the time is noted which the gold-leaf takes to reach a certain point on the scale of the micrometer.

Becquerel first announced that the rays given out by uranium exhibited the phenomena of polarization, reflection, and refraction, but this was not confirmed by other observers and on repeating his experiments with radium and with polonium Becquerel got contradictory and negative results. The French chemist observed that the rays emitted by different bodies are very unequally absorbed; the rays of radium and uranium freely penetrate plates of quartz, fluorite, and mica, but those of polonium are absorbed by these minerals and scarcely penetrate paper. On the other hand rays of polonium pass through aluminum more freely than those of uranium.

The rays of divers origin are also influenced in different ways by a magnetic field; in an irregular magnetic field formed by a powerful electromagnet, the rays emitted by radium are deflected and concentrated on the poles; to show this, Becquerel devised ingenious experiments giving photographic records.¹ On examining the rays of polonium compounds (furnished by Mme. Curie) he found that polonium acted differently from radium,² and his results failed to confirm the observations of Geisel previously announced. Later, Mme. Curie also published a note on the dissimilar behavior of the rays of polonium and of radium in a magnetic field.³ The subject has also been studied at Vienna by Stefan Meyer and Egon R. von Schweidler.⁴

Becquerel rays excite phosphorescence in gems, minerals, barium sulphide, calcium sulphide, etc.; in fluorite the phosphorescence remains twenty-four hours after the influence of radium has been removed, much as when exposed to the light of the electric arc.

In studying the power that these rays have of communicating energy to inactive bodies, Mme. Curie worked with substances so well purified that they were 50,000 times more powerful than uranium, and the induced activity measured 1 to 50 times that

¹ *Compt. rend.*, 130, 996, Dec. 11, 1899.

² *Ibid.*, Dec. 26, 1899.

³ *Ibid.*, 130, 73, Jan. 8, 1900.

⁴ *Phys. Ztschr.*, 10, 113.

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of uranium; the substances examined were zinc, aluminium-foil, lead, platinum, bismuth, nickel, paper, barium carbonate, and bismuth sulphide. Her experiments showed that true induction of radiant energy is effected, and the energy imparted to metallic plates is not removed by washing with water although the radium chloride ("chlorure de baryum radifère") is soluble. The activity induced by Becquerel rays persists, while that caused by Röntgen rays ceases suddenly on removal of the agent.¹

The actinic power of the rays is shown by exposing the same to sensitive plates; with the relatively pure material obtained by Mme. Curie an exposure of one-half minute sufficed to get an impression. The peculiar power of Röntgen rays is seen by using a barium platinocyanide fluoroscope, the rays exciting fluorescence through aluminum, vulcanite, etc.²

Mme. Curie records obtaining good "photo-impressions" with uranium, uranous oxide, pitchblende, chalcocite, etc. through glass, air, and aluminum.

The spontaneous luminosity of radium compounds was announced by Mme. Curie to the Physical Society of Paris in March, 1899,³ and in November of that year she published her discovery that the wonderful rays exert chemical action. They transform oxygen into ozone; this was first noticed by the odor of the air in a flask in which radium compounds were confined, and was confirmed by the usual test with potassium iodide and starch-paper. The rays also produce a certain coloration in glass changing it to violet; and they transform barium platinocyanide from yellow to brown, in which state it is less fluorescent, but this can be revived by insolation.⁴

At the suggestion of Mme. and M. Curie, M. A. Debierne, working in the laboratory of the Sorbonne, examined pitchblende for other radio-active bodies, especially the portion precipitated from solution by ammonia and ammonium sulphide, after separation of the uranium; in October, 1899, he found associated with titanium, a substance exhibiting 100,000 times more radiant power than uranium, and having chemical properties distinct from radium and polonium. The rays emitted by this body, named actinium, have the same manifold action as the other substances, with the exception that it is not self-luminous.⁵

In a more recent paper⁶ M. Debierne finds that actinium is

¹ *Compt. rend.*, 124, 714, Nov. 6, 1899.

² *Ibid.*, 126, 1101 (1898); 127, 1215, Dec. 26, 1898.

³ *Rev. chim. pure et appliquée*, July, 1899.

⁴ *Compt. rend.*, 129, 823 (Nov. 30, 1899).

⁵ *Ibid.*, 129, 593.

⁶ *Ibid.*, 130 (April 12, 1900).

allied to thorium, and suggests that the radio-activity of the latter is due to admixture of the new substance.

To complete this review of the radio-active bodies, brief notice must be made of two papers by German chemists. Fritz Geisel obtained radium from uranium ores other than pitchblende, and remarks: "Freshly crystallized Ba salts containing Ra are only slightly active, but in a few days or weeks they reach a maximum. They are strongest when anhydrous, moisture stops activity and heating restores it."

Becquerel rays have the same intensity in partial vacuum as at ordinary air-pressure; this was proved by electrical and photographic experiments made by J. Elster and H. Geitel.¹

Through the enterprise and liberality of the Smithsonian Institution, and by the courtesy of Secretary Langley, I have enjoyed the opportunity of studying small specimens of these rare and costly substances; they comprise 10 grams of "radio-active substances" in two portions, prepared by E. de Haen, manufacturing chemist of Hannover, Germany, and 4 grams of "chlorure de barium radifère," and 4 grams of "polonium subnitrate" from the "Société Centrale de Produits Chimiques (Ancienne Maison Rousseau)", Paris, said to be prepared according to the instructions of Mme. and M. Curie.

The samples from Hannover were marked "A" and "B" respectively, and a memorandum accompanying them stated that "B" excites fluorescence in barium platinocyanide more energetically than "A," whereas the latter is self-luminous; as a matter of fact I found both luminous in the dark and "B" the brighter of the two.

The specimens were enclosed in hermetically sealed bottles and protected from light by straw-board cylinders; on removing the wrappings in a dark room both were seen to emit greenish white light that gave to the enveloping papers a peculiar glow, similar to the fluorescence produced by Röntgen rays. I here call especial attention to the fact that during all the time that I have had the substances under examination they have been kept in the dark, no light reaching them stronger than that of the yellow and orange-red of a photographic dark room, so that insolation has played no part in renewing their energy.

The grayish white powders proved to be wholly soluble in water and the solution gave the usual reactions for barium chloride.

Moistening the radium chloride with cold water does not immediately stop emission of light, but on heating to boiling, the luminosity ceases. The water was expelled and the material, heated in a platinum dish to dull redness, resumed its luminosity

¹ *Ann. Phys. Chem.*, 69, 91 (1898).

² *Wied. Ann.*, 66, 135 (1898).

after a few days *in the dark*. The fact that radium compounds resume their power of emitting light slowly has been noted Geisel, but he fails to state whether the salt regains its proper without exposure to sunlight.

The substances "A" and "B" were examined with a fluorescent screen at first without success, but in a perfectly dark room, after the eyes became sensitive, the screen of barium platinocyanide was distinctly seen to fluoresce feebly.

The small specimens of these bodies had no perceptible influence in exciting phosphorescence of sulphides of the alkaline earths exposed to their action.

Having at hand no apparatus for measuring the electrical conductivity of the air, my experiments were chiefly directed to ascertaining the action of the rays on sensitive plates.

The photographic experiments were made with Seed normal halation dry plates (No. 26). To test the approximate actinic power of the bodies "A" and "B," sections of sensitive plate at distances of 5 and 10 inches were exposed at intervals of from two to twelve minutes; these gave bands varying in intensity with the duration of action. "B" showed far greater power than "A". By exposing sensitive plates behind an ordinary negative to the entire 10 grams of "radium" from two to three hours, good transparencies were obtained; on substituting Eastman's bromide paper, prints were secured; the distance of the sensitive surfaces from the source of light was about 3 inches.

To get skiagraphic images, plates were enveloped in Carbutt's black paper (non-permeable to light) and on this was laid a piece of tin-foil cut in open work pattern; after one hour's exposure a negative was obtained plainly showing the pattern. "A" was apparently stronger than "B".

Analogous experiments were carried out with the specimens of "radium" and of "polonium" from Paris; making allowance for the difference in weight, the radium of German origin was about five times as active as the French. The sample labeled "polonium subnitrate" (weighing 4 grams), had positively no action on the plates used.

Having at my disposal 500 grams exceedingly well purified uranic nitrate (remaining from previous researches), I examined it for Becquerel rays, but a sensitive plate exposed three hours to the beautifully fluorescent crystallized salt gave no trace of action. Similar negative results have been obtained by Sir William Crookes.

The primary source of the energy manifested by these extraordinary substances has greatly puzzled physicists and as yet remains a mystery. Mme. Curie speculating on the matter, at first proposed the following explanation: she conjectured that all space is continually traversed by rays analogous to Röntgen

rays but far more penetrative, and not capable of being absorbed by certain elements of high atomic weight such as uranium and thorium.

Becquerel, reflecting on the marvelous spontaneous emission of light, remarked: if it can be proved that the luminosity causes no loss of energy, the state of the uranium is like that of a magnet which has been produced by an expenditure of energy and retains it indefinitely, maintaining around it a field in which transformation of energy can be effected. But the photographic reductions and the excitation of phosphorescence in a sensitive screen require an expenditure of energy, of which the source can only be in the radio-active substances. As this expenditure is slight perhaps the bodies have a large reserve of energy which can be drawn upon for years without showing loss; at any rate it has been impossible, says Becquerel, to bring about any appreciable variation in the intensity of the emission by physical influences.

Somewhat later Becquerel hazarded the opinion that the radiation of radium is composed at least in part of cathodic rays; but these have been proved to be material, hence the induced activity must be caused by material particles impinging upon the substances excited. This materialistic theory seems to be confirmed by the results of ingenious experiments made by Mme. and M. Curie; they placed a sensitive plate beneath a salt of radium supported upon a slab of lead, in the vicinity of an electromagnet. Under these conditions when the current was passing, the rays emitted by the chemical salt were bent in curved lines upon the sensitive plate, making impressions.

It may be objected, says a French writer in the *Revue générale des Sciences* that this theory requires us to admit actual loss of particles of matter, nevertheless the charges are so feeble that the most intense radiation yet observed would require millions of years for the removal of 1 milligram of substance.

The same writer raises the question, which of the observed phenomena is the primary one? does the radiation of radium excite cathodic rays, or do the latter exist in the chemical compounds? and he regards the latter as improbable. The primordial source of energy in radium probably resides, he adds, in the ultraviolet light, and the efflux of material particles that ensues is only a secondary phenomenon, but on a far larger scale than has previously been observed.

Speculations as to the future history and applications of these wonder-working bodies press upon even the dulllest imagination; if a few grams of earth-born material, containing probably only a small percentage of the active body, emit light enough to affect the human eye and a photographic plate, as well as rays

that penetrate with X-ray power, what degree of luminosity, of actinism, and of Röntgenism, is to be expected from an hundred-weight of the quintessence of energy purified from interfering matter?

And to what uses is this light-generating material to be applied? Are our bicycles to be lighted with disks of radium in tiny lanterns? Are these substances to become the cheapest form of light for certain purposes? Are we about to realize the chimerical dream of the alchemists,—lamps giving light perpetually without consumption of oil?

Seriously, in what direction is profound study of these substances going to lead us? Will it not greatly extend our knowledge of physical manifestations of energy and their correlation? What bearing will this power of "opening up paths through the air" for currents of electricity have upon our knowledge of heat, light, electricity, and those forms of energy called by the names of Röntgen and Becquerel?

In what corner of the globe will be found the cheap and convenient supply of raw material yielding the radio-active bodies? Will not chemists be obliged to reexamine much known material by laboratory methods conducted in the dark? Many of us have worked up kilograms of pitchblende to extract uranium oxides and in so doing have poured down the waste-pipe or thrown into the dust-bin the more interesting and precious radio-active bodies.

At all events whatever the future may bring, physicists are deeply indebted to Becquerel, and to Mme. and M. Curie for placing in our hands new methods of research and for furnishing a novel basis for speculations destined to yield abundant fruits.

POSTSCRIPT.

Bela von Lengyel, of Budapest, has pointed out that the chemical evidence is insufficient to establish the elementary character of these radio-active bodies, and claims to have prepared the so-called "radium" synthetically. By fusing with the heat of the electric arc uranic nitrate mixed with 2 to 3 per cent. of barium nitrate, and treating the mass with nitric acid, water, and sulphuric acid, successively, he obtained radio-active barium sulphate possessing all the physical properties characteristic of the "element" announced by Mme. Curie. The resulting substance gives out actinic rays, Röntgen rays, excites platino-cyanide screens, and causes air to conduct electricity.

The Hungarian chemist has made and examined the chloride and the carbonate of this substance and finds that they have the same properties; he wishes his paper regarded as a preliminary notice, proposing to continue his researches.

Von Lengyel's paper was received by the German Chemical Society on April 2nd, but the number of the *Berichte*¹ containing it only reached Washington on May 26.

Admitting that radio-active bodies can be manufactured to order, are we any nearer explaining their mysterious powers?

HENRY CARRINGTON BOLTON.

COSMOS CLUB, WASHINGTON, D. C., May 26, 1900.

MODERN RESEARCHES ON THE CHEMISTRY OF THE PROTEID MOLECULE.²

It is impossible, at the present stage of our knowledge, to give any satisfactory definition of a proteid, based either on its physiological or chemical properties. Physiologically, it can be pointed out as the main constituent of all cells and tissues. In regard to its chemical properties, it can be stated with absolute certainty that it consists of carbon, hydrogen, oxygen, nitrogen, and sulphur. It does not possess very marked acid or basic properties, but forms salts with both bases and acids, its affinity for both being very weak.

I.

It can not be classified under any of the well-established groups of chemical compounds. Some attempts in this direction, however, have been made in recent years; and of these, the attempt to classify all proteids among glucosides has been the cause of much dispute from the experimental and speculative side of the question. The author of this theory and its most enthusiastic advocate was Pavy, who, by hydrolysis of egg albumin, succeeded in obtaining a reducing substance, capable of combining with phenylhydrazine, forming an osozone of a definite melting-point.

Physiologists, who were all inclined to see the source of the tissue-carbohydrates in the tissue-proteids, naturally welcomed Pavy's work, and were ready to endorse his views. A number of researches, however, were undertaken in order to test the correctness of Pavy's statements. The results thereof were contradictory. Morner has investigated, in that direction, serum globulin, and found that on heating with 3-5 per cent. hydrochloric acid, it yielded a solution capable of reducing Fehling's solution. Krawkow has tested, in the same direction, various proteids with different results. Substances combining with phenylhydrazine, giving osozone, were obtained by him from

¹ Vol. 33, p. 1237, May 14, 1900.

² Read before the New York Section of the American Chemical Society, May 11, 1900.

egg albumin (m. p. 183° – 185° C.), fibrin (m. p. 182° – 184° C.), and serum albumin (m. p. 183° – 185° C.). He failed to obtain similar substances, or obtained them only in traces from serum globulin, lactalbumin, casein, gelatin, vitellin, and mucoid.

The work which followed that of Krawkow was done by Eichholtz and is instructive in many ways. Thus, in contradiction to Krawkow, he failed to obtain the carbohydrate from serum albumin and succeeded in obtaining it from serum globulin. Of greater interest, however, is the fact that he found in the white of the egg, besides the ovomucoid, a substance related to it, which he called "ovomucin."

In regard to the egg albumin, two other researches are of great importance: first, that of Weydemann, who obtained on treatment of egg albumin with a 10 per cent. solution of sodium hydroxide, a substance similar to "animal gum"; and secondly, the work of Spenser, who repeated, under Drechsel's direction, the experiments of Pavy. Spenser was very careful to remove all the mucoid from the white of the egg, and only used such methods as would exclude the contamination of the egg albumin with the carbohydrates of the filter-paper, etc. Under such conditions, Spenser failed to obtain a carbohydrate on the hydrolysis of egg albumin with acids.

A comparison of the results of all the authors reveals the fact that proteids of the same nature gave different results to different investigators, as can be seen from the following table:

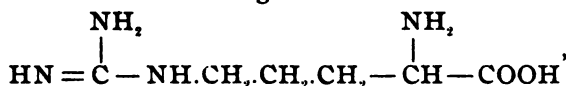
	Pavy.	Krawkow.	Eichholtz.	Morner.	Spenser.
Egg albumin	positive	positive	positive	negative
Fibrin.....	"	"	"
Serum albumin ...	"	"	negative
Serum globulin ...	"	negative	positive	positive
Lactalbumin	"
Casein	positive	"
Gelatine	negative	"
Vitellin.....	positive	"
Mucoid	"

Further, new substances related to mucins were discovered where they were not suspected by some of the investigators searching for carbohydrate in the proteid molecule; and finally, those who were more careful in avoiding contamination were the least successful in obtaining the "carbohydrate moiety" of the proteid molecule. It seems therefore unwarranted at the present moment to accept the existence of such a moiety.

II. THE NITROGEN.

The greatest part of the researches on the chemistry of proteids has been directed to the character and form of the nitrogen present in its molecule. The older authors knew that the nitro-

gen was not all in equally strong combination with the rest of the proteid molecule, and that the nitrogen entered the proteid molecule in the form of an amido group. But of the amido compounds only those of the monamido acids were detected in that molecule. A great part of the nitrogen was in a combination unknown to most of the old investigators. Drechsel was the first to investigate with great success the nature of the nitrogenous residue. He has found that it consists of substances with a well-defined basic nature, some of them being diamido acids. The substances he discovered were lysin and lysatine: one being diamidovalerianic acid, $C_6H_{14}N_2O_2$; the other a homologue of creatine, $C_6H_{13}N_3O_2$. Later he also discovered among the decomposition products of proteids diamidoacetic acid. A number of different proteids were examined by the students of Drechsel, namely, E. Fisher, Siegfried, and Hedin, and the presence of the bases lysin and lysatine was demonstrated in all of them. Furthermore, Siegfried isolated besides these two bases, a new one having the composition $C_{11}H_{20}N_6O_6$. Hedin then obtained, by the decomposition of different proteids, arginin, a base of the following formula :



and which was first described by E. Schulze as a constituent of vegetating seeds. Later Hedin also demonstrated that the substance, described by Siegfried as $C_{11}H_{20}N_6O_6$, was histidin- $C_6H_9N_3O_2$ —a base first discovered by Kossel as a decomposition product of a protamine, "sturin."

The statement of R. Cohn that a pyridin base could be detected among the other basic decomposition products of the proteids was very recently retracted by him.

After the presence of the basic substances in the proteid molecule was demonstrated, the question arose, how are they grouped in the molecule? and the researches of Kossel seemed to fully answer it. Kossel has resumed the work of Miescher on protamines—substances occurring mostly in fish sperm in combination with nucleic acid. The protamines had some properties common with proteids; namely, they gave the same color reaction with an alkaline copper solution as the proteids, a test known as the "Biuret test," undergoing also the same changes in solubility as proteids on digestion with pepsin hydrochloric acid.

Finally they yielded on decomposition the basic substances met with on decomposition of other proteids. The points of difference were that the protamines did not give the other color tests peculiar to proteid material and did not contain the other decom-

position products met with on decomposition of proteids except the "hexon" bases. The conclusion was natural that the property of the proteids to give the biuret test was due to the presence in its molecule of a protamine group. Such actually was the conclusion of Kossel, and, according to his theory, the protamine is the nucleus of all proteids in the same manner as benzene is the nucleus of all the aromatic compounds.

On further investigation, however, it was found that only one protamine, namely sturin, yielded, on hydrolysis with acids, all the three "hexon" bases, sturin yielding as well amidovalerianic acid. The other protamines, such as clupein, scombrin, salamin, yielded only arginin, amidovalerianic acid, and an unknown residue. Cycloxytelin contained besides these an aromatic group. Thus it appeared that the biuret color test is not peculiar to one certain "protamine group," and from this standpoint there is no reason to believe that all the proteids are derivatives of one protamine.

The analysis of animal proteids by Larrow and of plant proteids by Schulze, Mendel, and Levene, which have been made up to the present time, have revealed in all of them the presence of the three hexon bases. This would seem to corroborate the view that in proteids the biuret reaction is due to a "protamine." An objection to the latter assumption, however, can be found in the researches of H. Schiff.

H. Schiff has demonstrated that the biuret reaction can be obtained from different substances which contain two CONH_2 groups combined together, either directly, like oxamide $\begin{array}{c} \text{CONH}_2 \\ | \\ \text{CONH}_2 \end{array}$ or joined on a single carbon or nitrogen, like biuret $\text{NH} \begin{array}{c} \text{CONH}_2 \\ \text{CONH}_2 \end{array}$ or malonamine, $\text{CH}_2 \begin{array}{c} \text{CONH}_2 \\ \text{CONH}_2 \end{array}$ Another requisite is that the CONH_2 groups be combined in an open chain.

Thus H. Schiff has established the fact that the property giving the biuret color test is peculiar to more than one substance, that this property is due to the presence in the molecule, not of amido groups or amido acids, but of two of the radical CONH_2 grouped in a certain way; that it is not very probable that a combination of "hexon" bases (which, according to Kossel's first surmise, constituted the protamine molecule) will necessarily give the biuret test; that, finally, in the protamines as well as in other proteids the peculiar color formed on addition of alkaline copper solution is due to the presence in their

respective molecules of a substance common to all of them, possibly, but perhaps not yet discovered. Attempts were also made to estimate the quantities of the different nitrogenous compounds in the molecules of different proteids, so as to establish a basis for their chemical classification. Hansemann has analyzed with this in view a great number of proteids, finding that the proportion of these constituents varied greatly with the character of the proteid. Henderson has, however, demonstrated that the temperature and the duration of the decomposition has a great influence on the formation of the different nitrogenous constituents, and thereby the conclusions of Hansemann lose much of their weight.

III. SULPHUR.

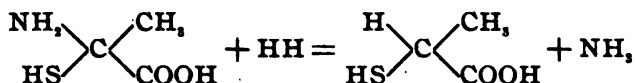
It has been accepted that the proteid molecule contains more than one atom of sulphur, and that the different atoms are in different forms of combination. This view is based on the fact that proteids heated with a solution of sodium hydroxide generally gave up part of their sulphur in the form of hydrogen sulphide, and the rest of the sulphur was detected only by means of strong oxidation, like fusion with sodium hydroxide and nitrate. Attempts have been made to establish the ratio between the different atoms. However, the methods employed by the older authors were not faultless, as the possibility of an oxidation of a part of the hydrogen sulphide into sulphuric acid (on heating with sodium hydroxide) was not excluded. The question thus needed new consideration, and such was given to it by F. N. Schultz. Great care was taken by the latter to prevent the possibility of oxidation of hydrogen sulphide, and in most experiments only about one-third of the total sulphur could be obtained in the form of hydrogen sulphide.

Very little has been known in regard to the nature of that part of the sulphur which could not be obtained as hydrogen sulphide. The opinion that it is in an oxidized state has been proved to be erroneous.

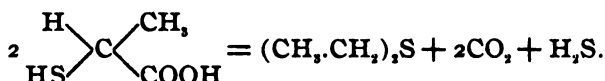
In recent years a few researches have appeared which throw some light on the subject, although none of them gives a final solution to the problem. Drechsel found among the basic decomposition products of the proteids, a substance which, on treatment with alkalis, yielded ethyl sulphide. He, therefore, concluded that the substance must be a sulphin base or a thetin compound; and that a quadrivalent sulphur was present in the proteid molecule.

A short time after Drechsel's discovery, Suter working in Baumann's laboratory, isolated from the decomposition products of proteids thiolactic acid, and very recently Morner has suc-

ceeded in obtaining, under the same conditions, cystein, which is a derivative of the former, as can be easily seen from the formulas.



Baumann has demonstrated further that similarly to the thetin compounds, the cystein or thiolactic acid yields ethyl sulphide on treatment with alkalies, according to the following formula :



Thus, another explanation was offered for the appearance of ethyl sulphide among the decomposition products of proteids. It must be remembered that both the substances ethyl sulphide and cystein (cystin) had been detected in animal secretions long before they could be obtained directly from proteids. The former was first identified in the urine of a dog by J. Abel; the latter by Baumann.

HALOGEN PROTEIDS.

Considerable study has been devoted to the halogen derivatives of the proteids; it was expected that the latter compounds would be of great aid in explanation of the constitution of the proteid molecule. The expectations, however, have not been realized up to the present date; although the future may be more successful.

SYNTHESIS.

Notwithstanding that little regarding the chemical constitution of the proteid molecule is established, attempts have already been made to obtain a proteid synthetically. In recent years the attempt was made by Lilienfeld, who stated in 1894 that he was successful in obtaining a synthetical proteid in the following way :

Curtius and Goebel found that if glycocoll-ethyl ester was allowed to stand, it yielded glycocoll and a biuret-giving substance which Lilienfeld claimed could form a condensation product with the ethyl ester of leucin, tyrosin, or aspartic acid, which product resembled peptone very closely.

More recently, Lilienfeld has modified his method and obtained proteids on condensation of phenol with glycocoll or with asparagin, etc.

Klimmer, however, justly remarks that Lilienfeld's substance could scarcely be considered a peptone on the following grounds :

1. The substance obtained by Lilienfeld yields readily, on decomposition, phenol and glyocol which other proteids do not, and the color which the substance takes, on treatment with alkaline copper solution, is not a color resembling the biuret reaction very closely.

Thus, little progress has been made towards the elucidation of the chemistry of the proteid molecule and its various parts. Attempts have been made to determine the weight of the molecule as a whole. According to Sabanejeff and Alexandrow, it is 14,900.

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THE PRESENT CONDITION OF THE COAL-TAR INDUSTRY.¹

As the end of the century approaches it is interesting and instructive to look back and note the wonderful growth of the chemical industries and the great changes they have undergone, especially in the last few years, in which many of them have been revolutionized.

It may be of interest to some to consider the growth and present condition of one of the greatest of these, that of coal tar and its products.

This industry which originated in the endeavor to utilize a troublesome by-product, has grown to be the one which without doubt employs more scientific men in its study and development than any other, and a description of all its products and their manufacture would be a review of the greater part of the organic chemistry of to-day.

About 1822 coal tar was first distilled in England, but it was not until 1856, the date of the discovery of the first aniline colors, that the industry became an important one; and it is in the last twenty years only that it has attained its present gigantic proportions.

At first the entire supply of tar was derived from the distillation of coal in the manufacture of illuminating gas, but under the constantly increasing demand, new sources have been developed, and these latter may in time become our main supply.

The coal tar produced in modern gas plants is quite different from that of some years ago. Cast-iron retorts were then used and the temperature of carbonization was comparatively low. The tar in consequence was generally quite fluid and contained considerable toluene, xylene, and phenols, some naphthalene and free carbon. With the introduction of fire-clay retorts, a marked change was noted and to-day the extreme high heat produced by the use of regenerators yields a tar which, considered from the standpoint of the distiller, is of much poorer quality.

The aim of the gas manufacturer is to get the largest amount of gas of good quality that can be obtained from the kind of coal carbonized. The high temperatures employed to do this cause the volatile products as they are evolved during the distillation to be decomposed in contact with the intensely heated sides of the retort with separation of free carbon, and, as exhausters are universally used, this is drawn out with the gases and deposited with the tar.

¹Chairman's address at the annual meeting of the Philadelphia Section, May 17, 1900.

The higher phenols and hydrocarbons are split up with formation of large quantities of naphthalene; therefore, the tar is heavier in gravity and thicker in consistency on account of the presence of more naphthalene and carbon and less of the liquid portions.

As the use of coal-tar products became more general, the demand for tar increased and in consequence the price advanced. The supply being to a certain extent fixed, manufacturers were stimulated to look for other sources of supply. Several plants were built in Europe and one in America having the production of tar and ammonia as their chief aim, but these were soon found to be unprofitable. Attention, however, had been called at an early date to the waste of these by-products in the manufacture of coke, and inventors without number entered the field with ovens designed to produce a good coke and at the same time save the tar and ammonia. A number of these, varying in minor details of construction, have been found to work well in practice,—besides, many beehive ovens have been provided with condensing plants for collecting the by-products. The tar obtained from these latter ovens and also from the gases of blast-furnaces is, however, quite different in composition from that obtained from gas works or improved coke ovens.

The temperature at which the coal is carbonized in the former being much lower, the tar contains practically no aromatic bodies, and when distilled yields oils which are free from naphthalene, benzene, and phenol, but instead contain compounds of the paraffin series, large amounts of higher complex phenols and paraffin; such tars are, therefore, of no value to the manufacturer of refined coal-tar products.

In the United States, owing to the extended use of oil and carburetted water-gas, the output of coal tar has been very much less in proportion to the population than in Europe, and it has been heretofore necessary to make up the deficiency by importing creosote oil and pitch. In the last few years, however, there has been a considerable addition to the domestic supply. A number of beehive ovens have been fitted with condensing plants and large batteries of improved coke ovens have been erected, and from these a fine grade of coke and considerable tar is obtained. The American coals appear to be much richer than those carbonized abroad.

In these ovens none of the charge is burnt to supply the heat necessary for the carbonization, as is the case with the older forms of ovens, and therefore, the yield of coke is very much larger, and may even amount to more than the analysis of the coal would seem to warrant, this being due to the deposition of carbon on the surface of the coke by the decomposition of a part of the tar as it is distilled.

The fact of a larger yield and purer quality of coke must, it seems, finally force other manufacturers to adopt improved ovens, and if even a part of the 20,000,000 tons of coke yearly produced in this country was made in such ovens with recovery of tar, we would pass from the condition of a shortage of supply to a veritable flood of tar, for even a small portion of which there would not appear to be a market.

One of the forms of ovens successfully introduced is the Semet-Solvay, of which about 300 are in operation in this country. Those interested in the subject will find a full description of them in an article by J. D. Pennock, which appeared in this Journal¹ in 1899.

The Otto-Hofmann ovens are used very extensively abroad, and through the kindness of Dr. Schniewind, chemist of the company, I am informed that 680 ovens are in operation in the United States, and that 400 are now being erected in Canada. The most interesting of these plants is that at Everett, near Boston, Mass., where 400 ovens are in successful operation. These have been fully described and illustrated by Dr. Schniewind in articles which have appeared in the *Progressive Age*. The plant is so situated that coal from Nova Scotia can be discharged directly from the steamers, and labor is reduced to a minimum by the use of every modern appliance for handling the materials used and produced.

The gas as it distils being higher in candle-power in the first hours of carbonization, this portion is collected by itself and after removal of tar and ammonia, is supplied to the city of Boston and vicinity. The gas coming off in the latter part of the distillation is used, after the tar has been removed, to heat the ovens. The coke is equal in quality to the best metallurgical coke and is sold for this purpose or broken into various sizes for domestic use.

It would seem that this novel and interesting application of the coke oven is destined to come into general use for large cities.

The tar from these ovens resembles the average retort tar except that it does not contain as much low-boiling hydrocarbons or phenol.

A certain amount of tar is also obtained from the manufacture of oil- and water-gas but they are of much less value than pure coal tar. The water-gas tar is especially difficult to utilize as it contains from 50 to 75 per cent. of water in the state of an emulsion which will not separate on standing.

In the United States tar is usually distilled into light oil, heavy oil, and pitch. The light oil comprises the first portions of the distillate until the oil, as it runs off, sinks in water. The

¹ This Journal, 21, 678.

entire distillate when mixed has a gravity from 0.93 to 0.98. Its nature has varied with the change in the tar as noted above, formerly they were quite fluid, but now in most cases they are semisolid from naphthalene.

The pitch remaining in the still after the distillation is known as soft pitch, and is adapted for roofing or paving purposes.

Formerly it was customary to run to hard pitch which was sent abroad to be used in the manufacture of compressed fuel; the anthracene oil obtained by this distillation was filtered and the anthracene pressed in hydraulic presses, making 40 per cent. anthracene. This was shipped to England and used in the manufacture of alizarin. At that time anthracene was one of the most valuable of the crude tar products, but the price has now fallen so low that it does not pay to export it, and there is very little sale for hard pitch as the manufacture of briquettes for fuel is carried on in a limited way only. The manufacture of anthracene has, therefore, been abandoned for some years.

The demand for creosote oil has, on the contrary, been constantly increasing owing to its extensive use in creosoting lumber, a number of plants for this purpose being in operation here.

Oil for this purpose is required to conform to certain specifications; formerly it was deemed necessary to have a large amount of tar acids, but now it is recognized that the naphthalene is a much more important agent in the preservation of lumber; and in consequence, specifications require 40 to 50 per cent. to be present, and in cold weather the oils are often entirely solid from separated naphthalene. In this connection, it is well to call attention to the fact that many specifications call for 50 per cent. of naphthalene and yet require the oil to be limpid at 90° F., which is an impossibility when such a large amount of naphthalene is present.

When we come to consider the refined products of coal-tar we can, in the short time at our disposal, mention only the most important. In general it may be said that each year greater purity is demanded by consumers, and a large number of the commercial products are practically chemically pure.

This branch of the industry has not made as great strides in the United States as it should. A severe blow was dealt when nearly all the protective duties were removed a few years ago. Formerly there was on the most of them a duty of 20 per cent. which enabled the American manufacturer to compete notwithstanding the higher wages ruling here.

The use of special labor-saving machinery which has done so much to enable our manufacturers to enter the markets of the world is not an important factor in this industry, which, owing to its nature, does not permit the extensive use of such labor-

saving devices, and where machinery can be used, we find the German manufacturers, who are our chief competitors, have the most improved devices in this line.

If we compare the estimates of cost of manufacture by American and German experts, the item of labor is seen to be a very serious one. For ordinary labor we must pay from 14 to 15 cents per hour, German estimates are based on 6 to 7 cents. In the pay of skilled mechanics the difference is even more striking: carpenters, masons, machinists, boiler and tank makers, receive from 30 to 45 cents per hour, while the prices abroad are scarcely 50 per cent. of these. This has a twofold effect on the industry: first, in increasing the item of repairs and maintenance, which, owing to the nature of the business, is a very large one, necessitating the constant renewal of parts destroyed in the processes. Second, it handicaps the manufacturer by requiring a larger outlay of capital to erect the plant than is the case abroad. A conservative estimate would be that an average plant would cost twice as much here as in Germany.

Of all the refined products, benzene has probably been subject to the greatest fluctuations. The demand for this article increased so rapidly that the price became very high, and efforts were made in all directions to perfect processes which would produce it independently of the gas works. It was at this time that the endeavor was made both in Europe and America to distil coal in retorts at the mines with the making of benzene as their prime object; but, as already stated, these were soon abandoned. A plant was also built in Ohio to manufacture benzene and its homologues from petroleum residues but without success.

Attention had been called at an early day to the large amount of benzene present in the coal gas, amounting to about twenty times as much as is present in the tar from the same gas. It was manifestly impossible to remove it from the gas without destroying, to a large extent, its illuminating power, but this objection did not hold good with the gas obtained from the improved coke ovens, and appliances were added to these plants to remove this benzene. A large number of such plants are in operation abroad at this time; the gas from the ovens after removal of tar and ammonia is forced through specially designed towers, in which the gas is brought into intimate contact with a fraction of oil from coal tar. This oil absorbs the benzene, and when saturated, is heated, and the crude benzene driven out. The product thus obtained is equal to about 90 per cent. benzene; that is to say, consists of about 70 per cent. benzene, 20 to 25 per cent. of toluene, and the balance of higher bodies. The introduction of these benzene extracting plants may be said to have been *too* successful, as the price has fallen to such an

extent that the extraction at present is hardly remunerative. We are, however, assured of a source of supply which can be readily increased as the demand warrants. The present supply is undoubtedly more than the demand; toluene, however, is not obtained in such large quantities by this method and as the demand is steadily increasing owing to many new uses, among them the manufacture of artificial indigo, the price has advanced so that it is now selling abroad at a higher price than benzene, while formerly the reverse was the case. At the present time there is no plant in operation in this country extracting the benzene from gas.

The low price of benzene permits it to be used in many industries as a solvent for the extraction of chemicals and drugs, and immense quantities are used abroad for enriching gas.

Naphthalene is one of the coal-tar products which is now manufactured on a very large scale in a great degree of purity. This article has advanced considerably in price owing both to the great demand, and to the fact that crude naphthalene is now readily sold without removal from the creosote oil for reasons stated above. Before the duties were removed, there were three factories manufacturing the article in this country; since it has been placed on the free list only one of these survives. The output is chiefly used as a substitute for camphor for destroying moths.

Crystal carbolic acid or phenol is one of the few tar products which has not suffered the general decline.

In all the varied new sources of supply of other tar products, none has been found which promises increased output of phenol. The coke oven tar does not appear to yield much phenol, so that while the supply is constant or perhaps increasing slightly, it does not keep pace with the large demand, the chief of which is for the manufacture of picric and salicylic acids. A limited amount of phenol is made in this country, and considerable refined from imported materials, but the great bulk comes to us in a finished condition from Europe.

Nitrobenzene, nitrotoluene, and other nitro compounds are made in one factory, the output being mainly used by manufacturers of colors and explosives. A certain quantity of rectified nitrobenzene, known as oil of myrbane, is used by manufacturers of soaps and oils.

Aniline oil which is made in such large quantities abroad is not made at present in this country. Its manufacture was undertaken a number of years ago by makers of colors but abandoned as it was found the article could be imported at less cost. A factory, however, is now being equipped for its manufacture, and in a few weeks will be in operation.

Acetanilide is made by two or three factories and they supply nearly all the requirements of this market.

When the tariff on coal-tar products was revised and most articles placed on the free list, for some reason, salicylic and benzoic acids were 'singled out from all other compounds and favored with the specific duty of 10 cents per pound. In consequence, a number of works are now producing the former acid, using imported phenol.

The finer organic compounds are apparently not produced except vanillin, which is being made by at least two if not three firms.

Notwithstanding the great competition of Europe in aniline colors, the American manufacturers have in the last few years made decided strides, although as yet they appear to have confined themselves to the older standard colors. They are aided by a duty of 20 per cent. with practically all their raw materials free. They still labor, however, under the disadvantage of having to import a great deal of their supplies. There are at present five factories in operation.

It will be seen from this rapid review that there is still a wide field for the chemist and manufacturer in this country; and with a gradual increase in the output of crude materials, it is to be hoped and expected that in a few years we will produce a large amount of the enormous quantity of these products now imported.

England appears to have fallen out of the race in the competition for the American trade, especially in the finer coal-tar products, and Germany is now in the lead, even competing with England in the cruder preparations. To show the important position held by Germany, attention is called to the statistics compiled by the German government up to July 1898, on which date there were 25 factories devoted to anilin and anilin dyes, and 48 establishments which made dyestuffs, carbolic acid, and other coal-tar preparations. Among the exports for 1898 were:

9,321 metric tons, alizarin,

19,712 metric tons, coal-tar colors.

12,360 metric tons, aniline oil and salts.

In this latter class the exports of 1898 were nineteen times as much as in 1883.

H. W. JAYNE.

NOTE.

Qualitative Tests for Boracic Acid.—It seems not to have occurred to authorities on the subject to test the effect of the alcoholic vapors of boracic acid on turmeric paper. We find that, if the test is applied in the following manner, the presence of boracic acid in minerals is rendered more certain and delicate.

Use a test-tube about 2.5 cm. in diameter and 20 cm. long. Put into the tube about 0.1 gram of the substance, 0.5 cc. hydrochloric acid, and 10 cc. wood alcohol. Boil vigorously down to small bulk, agitating the lower end of the tube in flame of burner, and holding the moistened end of a piece of turmeric paper just outside the mouth, so as to catch the vapors. Boracic acid will finally color the turmeric a characteristic red. Now, if the turmeric is placed vertically on the side of a beaker so as to dip into a little distilled water to which a few drops of ammonia have been added, a pinkish to deep purple or blue will be produced, in marked contrast to the red produced by the ammonia on the end of the paper unaffected by the vapors.

LOS ANGELES, CAL.,
July 2, 1900.

E. M. WADE AND M. L. WADE.

NEW BOOKS.

THE CALCULATIONS OF ANALYTICAL CHEMISTRY. BY EDMUND H. MILLER, Ph.D. New York: The Macmillan Co. 1900. viii + 183 pp.

In nearly all of the books published on the calculations of analytical chemistry there is a distinct statement in the preface that the book has been published with the idea of preparing the student to pass certain examinations. This pernicious system, fortunately, has not invaded the American text-book to anything like the same extent as it has the English books of the same class. There has been in the past scarcely any attempt to lay down general principles in regard to chemical calculations. This book is a decided advance in an attempt to treat the subject from a broad point of view. Just how far it will succeed remains to be seen, for there are hardly any two teachers who will treat the subject in the same way. All will, I believe, agree that it is a distinct advance to present such a subject entirely free from formulas. The student is asked to solve the problems, applying his general knowledge of chemistry. If he has been successful

in applying and understanding the laws, he can then construct his formulas if he so wishes.

The book consists of ten chapters divided as follows: calculations of chemical equivalents and atomic weights; formulae and percentage; mixtures having a common constituent; equations; use of factors; volumetric analysis; density of solids and liquids; gases; calorific power; electric and electrolytic calculations for direct currents. In addition there is a series of tables of weights, measures, specific gravities, factors, logarithms, etc., which will be found useful to any one having occasion to make any calculations. There will, probably, be a greater difference of opinion over the chapter on normal solutions than over any other. The author's development of the subject is satisfactory, but he has not exhausted the possibilities for clear treatment of a subject which can be made particularly attractive and instructive. The book, if used in connection with classroom work, will undoubtedly be of great value, and should help the student to a much clearer understanding of the quantitative values of chemical laws.

HENRY FAY.

COLOUR: A HANDBOOK OF THE THEORY OF COLOUR. BY GEORGE H. HURST. New York: D. Van Nostrand Co. 1900. Price, \$2.50.

The author of this book of 158 pages is a member of the Society of Chemical Industry, and is already known by his works on soaps, lubricating oils, painters' colors, and a "Dictionary of Coal Tar Colours." In this handsomely printed volume he endeavors to present to those familiar with the practical printing and dyeing of textile fabrics, and the mixing of colors for artistic effects, the theory of color, its cause and production, together with some account of the instruments used by scientific men in the study and measurement of color. The opening chapter treats of the prismatic colors, the spectroscope, wave motion, phosphorescence, fluorescence, luminosity, and so forth, in the compass of 31 pages. Other chapters deal with the theories of color as propounded by Young, Helmholtz, Brewster, and Maxwell, with the physiology of light, with contrast, and with the application of color to decoration and design. In his preface Mr. Hurst acknowledges his indebtedness to the manuals of Chevreul, Benson, Rood, and Church.

The book is illustrated freely, containing no less than 72 cuts and 10 full-page colored plates; unfortunately for readers the plates, many of which contain several figures, are simply numbered and bear no references to the pages on which the text occurs that explains the figures, or that the figures illustrate. The figures on plate IV refer to texts on pages 79, 105, 106, and 114, and yet the plate faces page 48, and no indication is given of these references. It is true that the plates should be regarded as illustrating the text, but if the latter is first examined it will be found that references are not much clearer; on page 63 a reference to "Fig. 2, Plate 3" should read "Plate II., Fig. 2," and that to "Fig. 3" of the same plate should read "Fig. 4." Throughout the book, the plates bearing Roman numerals are referred to by Arabic figures, and lack of uniformity in the sequence of "Plate" and "Fig." increases the confusion. This unhappy blemish prevents easy study of the brilliant plates, but can be corrected in a second edition. There is an index and the volume is well bound. H. CARRINGTON BOLTON.

A POCKET BOOK FOR CHEMISTS. BY THOMAS BAYLEY. New York: Spon & Chamberlain; London: E. & F. N. Spon, Ltd. Seventh edition. xii + 559 pp. Price, \$2.00.

This book is already well known to chemists. The new edition, according to the preface, has been "rearranged and to a large extent rewritten." In spite of this much is yet to be desired in the arrangement of the tables and many of them might be presented in a much simpler and more compact form. In the selection of matter, it seems to the reviewer, that the author has attempted to cover too much ground and that many of the tables are so seldom used and are so readily accessible to any one having occasion to use them that they could well be cut out, while others such as those under the sections X, alcohol, XI, beer, and XII, sugar, might well be left for the special pocket-books gotten out for these industries. Of course there is no objection to the insertion of these tables except that they add to the size of the book and make the useful tables less readily turned to. In spite of these defects the book contains much valuable information and many tables in every-day use by chemists.

RICHARD K. MEADE.

FIELD TESTING FOR GOLD AND SILVER. A Practical Manual for Prospectors and Miners. BY W. HAMILTON MERRITT. London: Crosby & Lockwood; New York: D. Van Nostrand Co. 16mc. x + 144 pp. Illustrated. Price, \$1.50.

This is a book for the prospector and contains full directions for such rough tests as can readily be used in the field. Part I (72 pp.) is devoted to assaying, Part II to practical mineralogy and geology, and Part III contains a glossary of useful mining terms and a list of common rock-forming minerals and rocks. The booklet is bound in flexible leather, and is of a size suitable for pocket use.

E. H.

THE MANUFACTURE OF VARNISHES: OIL CRUSHING, REFINING AND BOILING. From the French of Ach. Livache, extended and adapted to English practice by John Geddes McIntosh. London: Scott, Greenwood & Co. 1899.

This book contains some information about raw materials which may interest the novice, nearly half the space being devoted to this, the greater part of which is reasonably correct. The author has collected a good deal of somewhat antiquated chemical literature on resins, the value of which is well indicated by the luminous observation on p. 18 that "The data are of no value, except in regard to the variety of copal which is referred to; and this is exactly the point which the investigators have almost invariably omitted to supply;" and "of little or no value to the practical varnish maker." The book is equally remarkable for what it contains and what it leaves out. For example, no reference is made to the almost universal practice of hardening rosin with lime; and it would be hard to compress more ignorance of the facts and of modern literature on asphaltums into a sentence than the following: "In its composition this mineral (Manjak) is similar to the pitch of Trinidad, to the gilsonite of Utah and the Canadian albertite." Nothing is said about oil-soluble aniline colors, but the incorrect statement is made that indigo-carmin is soluble in oil (p. 86). The present reviewer is not competent to criticize the chapter on spirit varnishes, except on one or two points. Shellac varnish is said to be made by dissolving one part of shellac in 5 to 12 parts of alcohol; such a solution can not be sold in this country, and probably not in England; regular shellac varnish is made with

5 pounds of shellac to 6½ pounds of alcohol. Much is said about wax in shellac but none of the practical modern methods of removing it are given. A brief and valueless section is given to the important subject of asphaltum varnishes. The preparation of raw linseed oil is well described; but a lot of venerable and worthless recipes for bleaching it are given, reference being sometimes made to "water-white" or "colorless" oil, something never yet produced, even approximately. The author seems ignorant of modern methods of oil-treatment, the most recent one referred to being Hartley's, which had been known and abandoned in this country before Hartley patented it.

Aside from references to Mulder and Chevreul (not very new) the treatment of the subject of driers is unsatisfactory. The fact is that the essential thing is to get a certain amount of lead or manganese into the oil, it makes no difference whether we use oxides, borates, or anything else; the other factor is the temperature needed. Zinc and magnesia salts are of no value, and are long out of date. Contrary to the statement on pp. 263-4, this reviewer has made excellent driers of nickel and cobalt, but they are too costly.

The section on oil and resin varnishes is especially unsatisfactory. It seems as if the translator ought to have been able to get some valuable matter for this, since the English varnish-makers produce varnishes which are up to date and of great excellence; but such does not appear to have been the case. The curious statement is several times made that in melting resins it is better to work with small quantities, 3 to 5 pounds, because the discoloration, produced by contact with the metal of the melting-pot, is less. Both theory and practice ought to show that the larger the vessel and the amount of resin the smaller is the heating surface per pound of resin, and the less the discoloration. It is, therefore, possible to melt 125 pounds at a time, which is the common American practice, and make a paler product than can be made in the laboratory. Before the use of the thermometer in this work the varnish-maker had various tests of heat, such as dropping in a bit of onion peel, which would brown and shrivel, or a feather, which would curl up with the heat when the temperature had reached a certain

point; but this fried-onion and burnt-feather business has now gone out of practice, notwithstanding what is said about it in this treatise.

One of the chief authorities quoted is Violette. Now Violette worked about half a century ago, and if he ever knew anything about practical varnish-making, which is doubtful, his book is out of date; and this is the general verdict to be passed on this book. It is misleading to the student, and of no value to the varnish-maker.

A. H. SABIN.

BOOKS RECEIVED.

The Manufacture of Varnishes. Oil crushing, refining, and boiling, and kindred industries; describing the manufacture and chemical and physical properties of spirit varnishes and oil varnishes; raw materials; resin; solvents and colouring principles; drying oils, their extraction, properties, and applications; oil refining and boiling; the manufacture, employment, and testing of various varnishes. Translated from the French of Ach Livache, Ingenieur civil des mines. Greatly extended and adapted to English practice with numerous original recipes by John Geddes McIntosh. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1899. vii + 403 pp. Price, \$5.00.

Commercial Fertilizers. By J. H. Stewart and B. H. Hite.—Bulletins Nos. 63 and 65. **Sugar Beet Investigations in 1899.** By J. H. Stewart and B. H. Hite.—Bulletin No 64. West Virginia Agricultural Experiment Station, Morgantown, W. Va. 82 pp.

Field Testing for Gold and Silver. A Practical Manual for Prospectors and Miners. By W. Hamilton Merritt. London: Crosby & Lockwood. New York: D. Van Nostrand Co. 16 mo. x + 144 pp. Illustrated. Price, \$1.50.

Charbon (Anthrax). Further investigations and suggestions, with summary and conclusions. Second series No. 60, Bulletin of the Agricultural Experiment Station of the Louisiana State University and A. & M. College, Baton Rouge, La. 28 pp.

Bulletin No. 57.—**The Smuts of Illinois' Agricultural Plants.** 72 pp. Bulletin No. 58.—**Composition and Digestibility of Corn-fodder and Corn Stover.** 10 pp. Bulletin No. 59.—**Orchard Management.** University of Illinois Agricultural Experiment Station, Urbana, Ill. 26 pp.

Gardening under Glass. Bulletin No. 170. The North Carolina College of Agriculture and Mechanic Arts, Agricultural Experiment Station, West Raleigh, N. C. 24 pp.

Proceedings of the Twenty-fourth Annual Meeting of the Pharmaceutical Association of the State of South Carolina, held in Charleston, S. C., May 1 1900. 30. pp.

The Chemistry of the Metals. By J. H. Kastle, Lexington. 1900. vi + 198 pp. 8vo.

Annali del Laboratorio Chimico centrale delle Gabelle. Diretti dal Dr. Vittorio Villavecchia. Volume IV. Roma: Tipografia Elzeviriana di adelaide ved. Pateras. 1900. 528 pp.

The Apple Orchard.—Bulletin No. 49. Agricultural Experiment Station of the University of Missouri, Columbia, Mo. January, 1900. 21 pp.

An Outline of the Theory of Thermodynamics. By Edgar Buckingham, Ph.D. (Leipzig). New York: The Macmillan Co. 1900. xi + 205 pp. Price, \$1.90.

L'Eau dans l'Industrie. Par H de la Coudré. Paris: Vve Ch. Dudon, Éditeur. 1900. 496 pp. Price, 15 francs.

Inspection and Analysis of Foods.—Bulletin No. 86. 51 pp. Kentucky Forage Plants; analyses of Some Kentucky Grasses.—Bulletin No. 87. 68 pp. with 14 plates. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky.

Essentials of Medical and Clinical Chemistry, with Laboratory Exercises. By Samuel E. Woody, A.M., M.D. Fourth edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1900. viii + 243 pp.

An Ephemeris of Materia Medica, Pharmacy, Therapeutics, and Collateral Information. July, 1900. On Acetic Acid as a Substitute for Alcohol in Extracting the Active Principles of Some Official Drugs. By Edward R. Squibb, M.D. 10 pp.

Corn Culture in North Carolina.—Bulletin No. 171. The North Carolina College of Agriculture and Mechanic Arts, West Raleigh, N. C. May, 1900. 20 pp.

Twenty-third Annual Report of the Connecticut Agricultural Experiment Station for 1899. Part III.—Papers on availability of Nitrogen, fertilizers for forcing-houses, insect notes, on tobacco diseases and remedies, fertilization of melons, notes on Fungi, tobacco experiments, and vegetable proteids. New Haven, Conn. 1900. viii + 195 pp.

(1) H. R. 11350. A BILL to establish the National Standardizing Bureau. (2) Document No. 625, Letter from the Secretary of the Treasury, transmitting, with accompanying communications, a draft of a bill for the establishment of a National Standardizing Bureau. (3) Hearing before the committee on coinage, weights, and measures, House of Representatives, May 3, 1900. Superintendent of Document Room, House of Representatives, Washington, D. C.

THE JOURNAL

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THE RELATIVE VALUES OF THE MITSCHERLICH AND HYDROFLUORIC ACID METHODS FOR THE DETER- MINATION OF FERROUS IRON.¹

BY W. F. HILLEBRAND AND H. N. STOKES.

Received July 27, 1900.

AMONG determinations in mineral and rock analysis, upon the accuracy of which great stress is laid, is that of iron in the ferrous condition. It is of special importance because an error attaching to it affects in like degree but opposite direction the ferric iron that is also nearly always present. Up to about the year 1867, the only method for its determination giving at all satisfactory results was that of A. Mitscherlich,² depending on the decomposition of the mineral at high temperature by rather strong sulphuric acid (3 parts acid to 1 part water by weight) in a sealed tube from which air has been expelled, and subsequent titration of the ferrous iron by permanganate. When pure hydrofluoric acid became a commercial article, the above method gave place in large measure to one depending on the decomposition of the silicate by a mixture of dilute sulphuric and hydrofluoric acids at atmospheric pressure and a tempera-

¹ Published by permission of the Director of the United States Geological Survey.

² *J. prakt. Chem.*, 81, 116 (1860).

ture not above 100° C., care being taken as before to prevent contact with air.¹

It became known in the laboratory of the United States Geological Survey fully twelve years ago that the two methods generally give discordant results when applied to the same rocks, the Mitscherlich method in such cases always showing the higher figure for ferrous iron. With low percentages of iron the discrepancies were not very great, but they seemed, in general, to increase as the ferrous oxide rose, until, with a rock showing 10 per cent. ferrous oxide by the hydrofluoric acid method, the Mitscherlich method might give 12 per cent. Experiments with artificial ferrous salts threw no light on the subject, for both methods gave with them the same sharp and concordant results.

Until very recently no cause suggested itself whereby the discordance could be explained. In theory, the Mitscherlich method seemed perfect, and it was concluded that, given entire decomposition of all ferruginous minerals, the determinations made by it were nearer the truth than those by the hydrofluoric acid method. That the reverse is true in most cases, appears as the result of work done in this laboratory in an entirely different connection.

In the first place, it had been found by long experience that nearly all rocks carry small amounts of sulphides—pyrite, pyrrhotite, or both—often visible to the eye, but more often in such small amount as to escape direct observation. One of us (Stokes), in an investigation now in progress on the oxidizing action of ferric salts on sulphur, pyrite, and other sulphides, has found that this action is vastly more rapid and complete than has hitherto been suspected; that not only is the metal of the sulphide oxidized, but the sulphur to sulphuric acid as well.

The application of these observations to rock analysis shows that the presence of 0.01 per cent. of sulphur in any unoxidized form may produce a maximum error of 0.135 per cent. in the ferrous oxide determination and the not infrequent amount of 0.10 per cent. of sulphur will multiply this error by 10. One atom of sulphur (32) requires for its complete conversion into trioxide the oxygen of three molecules of ferric oxide (480), which then becomes six molecules of ferrous oxide (432). The

¹ J. P. Cooke: *Am. J. Sci.* (2), 44, 347 (1867).

case is still worse with the sulphide, since not only the sulphur, but its accompanying metal must be oxidized. The above percentages of sulphur evolved as hydrogen sulphide and fully oxidized would involve errors in the ferrous oxide determination of 0.18 per cent. and 1.80 per cent., respectively. The error caused by sulphides tends to become greater the more there is present of either or both sulphide or ferric salt. Now the highly ferruginous rocks usually carry more ferric iron than the less ferruginous ones, and they are often relatively rich in pyrite and pyrrhotite; hence the increased discrepancy between the results by the two methods, as the iron contents of the rock rise, is fully in accord with the above explanation.

The following experiments made by Stokes (somewhat out of their contemplated order in his investigation referred to) bear out the above statements most fully and show that the Mitscherlich method for rocks and all minerals which contain even a trace of free sulphur or sulphides is no longer worthy of a moment's consideration.

Experiment 1.—0.0010 gram pyrite was heated with 25 cc. of a sulphuric solution (1 part acid to 3 parts water by weight) of ferric ammonium sulphate (0.0470 gram of ferric oxide) in a horizontally-lying sealed tube for six hours at 175° to 195° C. All air had been carefully replaced by carbon dioxide. The pyrite had nearly disappeared, and titration with permanganate showed a consumption of oxygen equivalent to 0.0068 gram ferrous oxide. Complete oxidation of the pyrite would have required oxygen equivalent to 0.0090 gram ferrous oxide.

Experiment 2.—This was exactly like the first, except that 0.0013 gram pyrite was used. Permanganate was reduced equivalent to 0.0090 gram ferrous oxide. Had oxidation been complete the figure would have been 0.0117 gram.

It is quite possible that in both of these experiments the oxidation would have been complete had the pyrite been disseminated throughout a greater space in the tube, as is the case when rocks and minerals are treated, because of the presence of a gram or thereabouts of diluting quartz and silicates.

Had precisely similar experiments been made with rock powders carrying 0.10 per cent., and 0.13 per cent., of pyrite with

4.7 per cent. of ferric oxide and no ferrous oxide, the following erroneous results might have appeared :

	I.	II.
Ferrous oxide.....	0.68	0.91
Ferric oxide.....	4.00	3.76

To overcome the possible objection that the foregoing experiments were not conclusive as to the worthlessness of the Mitscherlich method in presence of sulphides because the concentration of the acid was very different from the normal, the following sealed tube experiments were made with acid of the normal strength (3 parts acid to 1 part water by weight) without any ferric salt, the belief being that the stronger acid, under the conditions of the experiment, would itself act as an oxidizer.

Experiment 3.—Pyrite 0.0016 gram. Three hours at 195° C. Solution only partial. Consumption of permanganate equivalent to 0.00117 gram ferrous oxide.

Experiment 4.—Pyrite 0.0032 gram. Twelve hours at 220° C. Solution perfect. Odor of sulphur dioxide apparent on opening tube. Consumption of permanganate equivalent to 0.01742 gram ferrous oxide.

Experiment 5.—Sulphur 0.0021 gram. Three hours at 195° C., and, as the sulphur had not disappeared, further six hours at 250° C. Entire disappearance of the sulphur. Consumption of permanganate equivalent to 0.01320 gram ferrous oxide.

Experiment 6.—Sulphur 0.0039 gram. Twelve hours at 220° C. Entire disappearance of the sulphur and strong odor of sulphur dioxide on the opening tube. Consumption of permanganate equivalent to 0.03619 gram ferrous oxide.

In experiments 4, 5, and 6, where decomposition was complete the consumption of permanganate is considerably less than theory requires, but this is explained by the escape of not a little sulphur dioxide on opening the tube. Had a ferric salt been present the consumption of permanganate would undoubtedly have reached that required by theory.

It might be supposed from the foregoing that a similar error would affect ferrous iron determinations by the hydrofluoric acid method. However, experiment has shown that with the amounts of sulphide usually found in igneous rocks their effect is negligible, though by increasing the amount of sulphide the

effect becomes more and more apparent because of the greater surface of pyrite exposed to the action of the ferric iron of the rock.

Under the conditions of the Mitscherlich method, on the other hand,—a temperature of 150° – 200° C., and even higher, high pressure, much longer time of action, and impossibility of escape of any hydrogen sulphide that may be formed,—the sulphur of the sulphides becomes nearly, if not quite, fully oxidized to sulphuric acid, at the expense of the ferric oxide in the rock, with the production of an equivalent amount of ferrous oxide in addition to that resulting from the iron of the sulphide itself.

In order to obtain quantitative data regarding the effect of pyrite on the ferrous iron estimation by the hydrofluoric acid method, the following tests were recently made by one of us.

Part of a fine crystal of pyrite was rather finely powdered and boiled out with dilute sulphuric acid, which extracted considerable ferrous iron, derived presumably from admixed or intergrown pyrrhotite, or from superficial oxidation of the powder, since a second boiling with fresh acid afforded a negative test for ferrous iron. After washing by decantation with water, followed by alcohol and ether, the powder was dried and further pulverized. A quarter of a gram of it, when treated with dilute sulphuric and hydrofluoric acids in a large crucible by the Cooke method for ferrous iron, then rapidly filtered through a very large perforated platinum cone fitted with filter-paper, required but two drops of a permanganate solution representing only 0.0032 gram ferrous oxide to the cubic centimeter.

That the error obtaining under the conditions prevailing in rock analysis might be ascertained, successive portions of one gram each of a hornblende schist free from sulphur and carrying 10.09 per cent. ferrous oxide as the mean of several determinations and 4 per cent. ferric oxide, were mixed in a 60 cc. platinum crucible with 0.02, 0.025, and 0.10 gram, respectively, of the above purified pyrite powder. This mixture was then treated with hydrofluoric and sulphuric acids as above, the water-bath being at boiling heat for one hour. The cooled contents of the crucible were poured into a platinum dish containing water and titrated rapidly nearly to an end. Then, in order to get rid of the pyrite, which would obscure the end-reaction by

its reducing effect upon the permanganate, the solution was filtered as above and in the clear filtrate the titration was carried to completion. The results were 10.02, 10.16, and 10.70 per cent. ferrous oxide. Inasmuch as the smallest of these three charges of pyrite was several times greater than what may be considered an unusually high amount for an igneous rock, it is very evident that for all practical purposes the influence of pyrite on the ferrous iron estimation by the Cooke method is negligible. At the same time, it is to be borne in mind that with increased content, either of ferric iron or of pyrite, an increased amount of pyrite will be attacked and that the extent of this attack is undoubtedly influenced by the degree of fineness of the pyrite powder.

All users of the method have noticed the rapid disappearance in hydrofluoric solutions, when titrating ferrous iron, of the pink color produced by an excess of permanganate. If much ferrous iron be present, many cubic centimeters of permanganate can be added without causing more than a transitory pink coloration. The solution takes on, however, in ever-increasing intensity, the red-brown color characteristic of manganic salts. It seems that manganous fluoride in acid solution is very susceptible to oxidation by permanganate, for the above-mentioned changes take place when permanganate is added to sulphuric and hydrofluoric acids containing some manganous sulphate.

WASHINGTON, July, 1900.

ON THE DIGESTION AND ASSIMILATION OF PENTOSE AND FURFUROIDS.

BY C. F. CROSS, E. J. BEVAN, AND J. S. REMINGTON.

Received July 16, 1900.

THE furfural-yielding constituents of plant tissues continue to be designated by the majority of observers as pentosans. It is probable, however, that the group of natural products thus constituted are of more varied characteristics.

It must be noted first that we have no specialized form of pentosane comparable with starch and that the substances described as such are products isolated by chemical processes in the laboratory and devoid of the well-marked individuality and properties of the hexose-anhydride. We are not aware of any

evidence upon which the individuality of the best known of the reputed pentosanes, *viz.*, "Holzgummi," has been finally established.¹ Generally this group of substances is investigated in terms of furfural, obtained by boiling with condensing acids; and the relation of this aldehyde to the pentoses is indirect and of course not exclusive. Several of the now well-known oxidized derivatives of the hexose-carbohydrates are similarly condensed to furfural; of these we can call to mind: (a) Glycuronic acid; (b) the osones or ketoaldoses obtained by Fischer from the osazones and more recently and directly by ourselves by the action of hydrogen peroxide on the hexoses;² (c) a number of imperfectly defined products of oxidation of the hexoses and their polyanhydrides obtained both by laboratory and natural processes.³

Lastly it must be noted that investigation has failed to identify the pentoses as such occurring in the plant and the conclusion generally accepted at this date with regard to their formation is that they are not direct products of the assimilation process but originate from hexoses by processes of oxidation or internal change.⁴

Complementary confirmation of the exceptional physiological relationships of the pentoses is also supplied by the facts (1) that they are entirely resistant to alcoholic fermentation (yeast) and (2) are not assimilated by animal digestion.

From this brief résumé of the present state of our knowledge we draw the following conclusions: (a) That the group of furfural-yielding constituents of plants may comprise in addition to pentosans, oxy-hexoses (respectively anhydride) representing intermediate terms of a complex hexosan-pentosan series; and in view of this probability we prefer as a group designation the term furfuroid, and (b) that such oxyhexoses may yield to yeast fermentation and to animal assimilation.

Since these furfuroids are constituents of cellular tissues the question of alcoholic fermentation can only be studied by way of the products of acid hydrolysis. In so far as these products are pentoses they resist fermentation. This has been finally

¹ "Kohlenhydrate," II, p. 202, Tollens.

² *J. Chem. Soc.*, 73, 463 (1898); Morrell Crafts: *Ibid.*, 75, 786 (1899).

³ *Ber. d. chem. Ges.*, 27, 1061; Krüger and Tollens: *Ztschr. angew. Chem.*, 1896, Heft 2.

⁴ "Kohlenhydrate," II, p. 60.

established by the very careful investigation of Tollens;¹ at the same time we and other observers have studied cases of yeast fermentation in which there has been a considerable disappearance of the furfuroids from solutions in which they exist in a more or less fully hydrolyzed form.

In his investigation of this result Tollens arrives at the conclusion that the disappearance of the furfuroids is accompanied by the appearance of acid products; also that this effect is not inconsistent with the view that the products reacting in this way are pentoses.² Still the question is by no means finally elucidated and the incompleteness of the present solutions of the problem involved should be recognized.

In regard to the problem of animal digestion and assimilation we have to notice the results of investigation from two points of view. The pentoses proper have been investigated by Ebstein³ who found that xylose is not assimilated, being voided in unchanged form in the urine and Salkowski⁴ whose observations on arabinose led to the following conclusions: "Von dem jeden Thiere eingegebenen 10 g. Arabinose wurde etwa 1/5 unverändert durch den Harn ausgeschieden: das Blut enthält wenig, die Muskeln reichlich Arabinose. In der Leber fand sich gewöhnliches Glykogen und nicht, wie gehofft ein Pentosan. Die Resorption der Arabinose erfolgt schnell u. vollständig."⁵

On the other hand the furfuroids of fodder plants have been investigated by a number of observers who have variously estimated the proportion digested at from 40-90 per cent. These numbers represent for the most part the percentage ratio of the furfuroids disappearing in the digestive process, but they do not attempt to deal with the further question of assimilation. This more elaborate problem has recently been solved in a typical case by O. Kellner and A. Kohler.⁶ Oxen were fed upon a rye straw which had been previously extracted by boiling with alkaline lye—the product containing:

78.6 per cent. Rohfaser with

31.1 per cent. Furfurol gebende substanz.

¹ Stone and Tollens: *Ann. Chem.* (Liebig), 249, 257; Tollens: *J. Fed. Ind. Brewing*, 1898, 451.

² Tollens: *Ibid.*

³ *Archiv. Pathol. Anat.*, 129, 401.

⁴ *Central bl. Med. Wiss.*, 1893, No. 11.

⁵ *Ber. d. chem. Ges.*, 1893, 896.

⁶ *Landw. Vers. Stat.*, 1900, 53, 1, 474.

This product was added to the "Grundfutter" specially designed "zur Deckung des Mindestbedarfes des Thiers". The following results were obtained: Of the total product 95.8 per cent. was digested, and of the total available energy, 63.1 per cent. contributed to the formation of flesh and fat. The "furfuralgebende Substanz" contributed its proportion to the result and generally the cellulosic substance thus prepared has approximately the same feeding characteristics and value as starch.

But we find no records of investigations in which the furfuroids have been previously isolated by processes of acid hydrolysis. In absence of such results the proportions determined above are open to the objection that they are complicated by the unknown factor of digestive hydrolysis. To further elucidate the problem, therefore, we have carried out feeding experiments with the complex of products obtained from brewers' grains by digestion with dilute sulphuric acid (1 per cent. H_2SO_4) in an autoclave at a temperature of 130° . Under these conditions the furfuroids are selectively attacked and constitute 80-90 per cent. of the total soluble extract. The products in this form we have previously investigated and have found to be fully hydrolyzed from the numbers for cupric reduction; *viz.*, 110-120 (dextrose = 100) and yields of osazones.¹

The acid extract is neutralized (CaCO_3), filtered and evaporated. On distillation with hydrochloric acid of 1.06 sp. gr., the extract yielded 39.5 per cent. furfural calculated to the total dry weight. To convert the product into a form in which it could be easily administered to the animal (rabbit) as a foodstuff, it was mixed with a strong solution of gelatin at 20°C . and then with sufficient bread to give, when cold, a solid granular product. With this artificial food was associated a due proportion of fresh vegetable food; *viz.*, carrot and cabbage. The experiments were conducted with the usual precautions, in parallel series, one animal receiving the diet as above, a second receiving this same diet less the artificial furfuroid constituent. The details of the experiment are published elsewhere and need not be reproduced here.²

¹ *J. Chem. Soc.*, 1897, 1001-1010.

² *J. Soc. Chem. Ind.*, 1900, April 30.

The results obtained established the following high proportion (per cent.) of digestion and assimilation of the total furfuroids of the mixed diet

96.4 98.4 97.3 96.4 94.5

which are certainly minimum numbers for the special group of furfuroids under investigation. No pentoses or other furfural-yielding products were present in the urine, which was examined from time to time.

It may be concluded from these results that the typical furfuroids of cereal tissues when fully hydrolyzed are digested and assimilated by the herbivora as completely as starch and its products of hydrolysis. In this respect they differ from the pentoses and their anhydrides.

In view of these results and the exceptional physiological history of this group of constituents of plant tissues, which is by no means fully elucidated, we consider the term "furfuralgebende substance," or more shortly "furfuroid" is to be preferred as a general designation, reserving the term pentosan for its strict use; *i. e.*, as applied to a pentose-anhydride ($\text{H.C}_5\text{H}_{10}\text{O}_5 - \text{MH}_2\text{O}$).

4 NEW COURT, LONDON, AND LANCASTER,
ENGLAND, May 10, 1900.

ESTIMATION OF PYRRHOTITE IN PYRITES ORE.

BY F. B. CARPENTER.

Received August 15, 1900.

SINCE the introduction of pyrites into the manufacture of sulphuric acid, industrial laboratories have been frequently called upon to make analyses of pyrites ores to determine their quality for manufacturing purposes. In order to determine the relative value of these ores it is not only necessary to determine their sulphur content, but it is also essential that an estimation be made of those sulphides, which are difficult to decompose in the furnace. Fairly satisfactory methods have been described for the determination of zinc, arsenic, copper, etc., but I have heretofore seen published no satisfactory methods for the estimation of pyrrhotite. It is well known by acid makers that it is difficult to get the sulphur from this material, especially in lump burners, and as it is contained in nearly all our domestic ores to

a greater or less extent, the importance of its presence should not be overlooked.

The usual method for the determination of pyrrhotite in pyrites is based on its magnetic properties, and briefly stated, is carried out as follows: About 25 grams of the material, ground to pass a 60-mesh sieve, is spread out on a piece of glazed paper, and a magnet of the horseshoe type is passed backward and forward through small portions at a time. As soon as the poles of the magnet are loaded with attracted material the bridge between them is broken down with the armature, so that as much of the mechanically retained pyrites as possible may be dislodged; then after striking the magnet several times sharply with the bare hand to further free the magnetic portion from the pyrites, the adhering substance is transferred to a clean sheet of paper; then another portion of the ore is treated like the first, cleansing and transferring the attracted part in the same way, and this continued until the whole amount has yielded all magnetic matter. The portion removed to the second paper is still far from pure, and the cleansing operation is repeated for a second and third time in the same manner as the first, except that the magnet is held at a sufficient distance to lift the material and not rub among the particles. The magnetic material thus obtained is weighed and sulphur determined in one-half to one gram. The percentage of sulphur existing as pyrrhotite is then calculated from the results by multiplying the percentage of magnetic material found in the ore by the amount of sulphur found in 1 gram of the same. The difficulties in working this method are no doubt apparent to all who have used it. Pyrrhotite is only slightly magnetic and is very difficult to separate from the non-magnetic ore. After following out the method just described with the greatest care it is impossible to remove all the pyrrhotite or to have the magnetic material free from pyrites. We have slightly improved the method in this laboratory by substituting the electromagnet for the ordinary style, but the results are still far from satisfactory.

The method which I am about to describe was worked out in this laboratory, and is based on the solubility of the two sulphides (FeS_2 and Fe_7S_8) in hydrochloric acid, FeS_2 having been found to be practically insoluble while Fe_7S_8 seems to be wholly decomposed.

Details of the Process.—Determine total sulphur and silica by the usual methods; also copper, zinc, etc., if they are present in appreciable amounts. Test for pyrrhotite with magnet, and if present proceed as follows :

Treat 2 grams of the sample (ground to pass a 100-mesh sieve) in an 8-oz. beaker, covered with a watch-glass, with 30 cc. concentrated hydrochloric acid, boil ten minutes, filter on a weighed Gooch crucible, wash successively with warm dilute hydrochloric acid, hot water, alcohol, and finally several times with small portions of carbon disulphide. Dry at 100° and weigh. Weight of residue = $\text{FeS}_2 + \text{SiO}_2$. $(\text{FeS}_2 + \text{SiO}_2) - \text{SiO}_2 = \text{FeS}_2$. The sulphur required to satisfy the iron in the resulting FeS_2 is subtracted from the total sulphur, and the remaining sulphur calculated to Fe_7S_8 (pyrrhotite). The details of the calculations are as follows: $\text{FeS}_2 \times 0.534 = \text{sulphur in FeS}_2$; subtract this from the total sulphur and multiply the result by factor 2.529; this gives the percentage Fe_7S_8 present in the ore. These calculations apply to ores containing only traces of other metals besides iron. If other metals are present in appreciable amounts due allowance will have to be made. Zinc sulphide will be practically all decomposed by the hydrochloric acid; the percentage of zinc found, will therefore have to be satisfied with the required amount of sulphur, and the sulphur thus used deducted from the total sulphur before other calculations are made. Chalcopyrite, on the other hand, is only partly decomposed by the treatment with hydrochloric acid. Thus for the accurate estimation of pyrrhotite it will be necessary to make copper determinations both in the residue and filtrate, and calculate the results to chalcopyrite, subtract the amount of chalcopyrite found in the residue from the total residue, and the amount of sulphur required to satisfy the percentage of copper in the filtrate from the total sulphur before making the calculations. If only a small percentage of copper is present with no other metals, approximate results may be obtained by using dilute acid (1 to 1) for treating the ore. The amount of copper dissolved out by this treatment will be so small that it may be overlooked in the determination. The whole percentage of copper in the ore is in this case calculated to CuFeS_2 , and deducted from the total residue. Copper may be determined very quickly and

accurately by the cyanide process as described by Ricketts and Miller. If other disturbing factors are present the method will have to be modified accordingly, but the method as described gives results sufficiently accurate for all practical purposes on the great majority of commercial pyrites ores. This process is simple, reasonably quick, and gives much more satisfactory results than the other methods we have tried.

Mr. S. H. Sheib who is connected with this laboratory has rendered valuable assistance in perfecting this method of pyrrhotite determination, and its success is largely due to his careful work.

LABORATORY VIRGINIA-CAROLINA CHEMICAL CO.,
August 1, 1900.

THE ESTIMATION OF FAT IN SWEETENED CONDENSED MILK.¹

BY JOSEPH F. GRISLER.

Received August 8, 1900.

CONDENSED milk, as its name indicates, is a more or less concentrated milk, prepared by evaporating or distilling off a large percentage of the water of the milk. The concentration is usually carried to a degree to meet popular taste and trade requirements, unless the law establishes a specified degree of condensation. Broadly, this class of milk may be divided into the sweetened and unsweetened condensed milk, the former containing a large per cent. of cane-sugar as sweetener and preservative. Aside from its general good qualities, the extreme precaution of cleanliness in the preparation of most of the condensed milks has added much to their popularity, so that the sale and consumption of these milks is assuming vast and rapidly increasing proportions. As an article of food it is therefore more frequently being made the subject of analytical inquiry to determine its quality and freedom from adulteration.

While certain manufacturers pride themselves in turning out a product of uniform color, consistency, and superior keeping qualities and purity, others have deliberately put adulterated goods on the market and were prosecuted and fined for the same.

The analysis of ordinary milk presents no particular difficulties

¹ Read at the Twenty-first General Meeting of the American Chemical Society, June,

to the experienced analyst, but there is an abundant and cumulative evidence to show that the correct analysis of sweetened condensed milk is difficult and has proved to be a stumbling block to the efforts of many chemists.

Thus, quite recently, an article "A Method of Analysis for Canned Condensed Milk,"¹ by F. S. Hyde, appeared as a "Contribution from the Havemeyer Laboratories of Columbia University, No. 6," and this article has obtained wide circulation.

The results of the analyses of the first 17 samples reported are so utterly out of harmony with the composition of commercial condensed milk that experienced analysts have only to refer to the method whereby the results were obtained to learn the cause of the faulty statements. It is the general experience that the easiest part of analytical work is the writing out of a method. Without going into the details of the article referred to, I would quote² the following, which has a decided bearing in the application of the food laws:

A law of New York State requires that no "condensed milk shall be made,—unless the proportion of milk solids shall be in quantity the equivalent of twelve per centum of milk solids in crude milk and of which solids twenty-five per centum shall be fats." Sec. 25, Chap. 143, L. 1894.

"Generally the amount of fat in condensed milk is less than ten per cent. of the whole, or less than twenty-five per cent. of the forty per cent. (more or less) milk solids of which the fat is a part.

"The original cow's milk used may be considerably above the legal standard and yet the degree of condensation be insufficient to bring the manufactured article within the requirements of the law. Under such conditions the manufacturer might be liable to prosecution, although the product might be perfectly wholesome."

In the writer's experience it is the rare exception rather than the rule for condensed milks to contain less than a proportion of 25 per cent. of fat in the milk solids.

If, as stated, milk above the standard required by law be used

¹ This Journal, 21, 439 (1899).

² *Ibid.*, 21, 444 (1899).

for the condensation, there could be no legal prosecution of a manufacturer since the concentration would not materially alter the ratio of fat to milk solids, and the section of law quoted does not define the degree of concentration. Therefore, whether condensed little or much, the "condensed" product would not be an infraction of the law quoted, and prosecution under the same is out of the question.

Aside from insufficient condensation, it is generally assumed that skimming or the removal of butter-fat is the principal temptation to defraud on the part of the manufacturer. To prove skimming, the first essential is the accurate estimation of the fat, assuming the per cent. of fat obtained to be butter-fat. That is to say, the mere finding of the required per cent. of fat, and ratio of fat to milk solids would not prove such milk unadulterated unless the fat found was actually butter-fat.

Attempts have been made to remove the butter-fat and substitute other fat for the same in condensed milk; hence, the allusion to butter-fat particularly.

In the unsweetened condensed milk the estimation of the fat presents no particular difficulty, especially since the introduction of the Adams' coil method,¹ when the necessary precautions are taken. The large surface over which the milk solids are spread in the paper, a minimum of 110 sq. in., offers a medium from which solvents ordinarily rapidly extract² the fat.

The coil method has found general favor among analysts and were it not for the inconvenience of preparing "fat-free" coils it would be *par excellence*, and with certain modifications, the best method for the purpose. The preparation of the coils is tedious, but where accuracy is required the previous extracting of the coils to be used must be resorted to, as the quality of paper varies, some lots containing considerably more extractable matter than others.

Chemists were quick to avail themselves of the advantages of the coil method and use it in the estimation of fat in sweetened condensed milk, for the large surface offered advantages to overcome the difficulties experienced and pointed out by Hehner,³

¹ *Analyst*, March, 1885.

² See Vieth: *Analyst*, 16, 127; Geisler: "The Relative Merits of the Wanklyn and the Adams Methods in the Estimation of Fat in Milk Analysis," this Journal, 12, 488-500.

³ *Analyst*, 4, 45 (1879).

who stated "that it is quite impossible to extract the fat from the total solids by means of ether, or benzoline, the large amount of cane-sugar effectually protecting the fat."

Adams' method was not available until some years later. In the light of recent published analyses of sweetened condensed milk, Hebner was a "martyr" considering the abuse heaped on him by the manufacturers for the analyses, for it will presently be shown that even the extreme advantages of the *coil method*, unless certain precautions are taken, has its pitfalls. In the application of the coil method it is customary among a large number of chemists to proceed as follows: Thus Cornwall¹ and Wallace² state in following out the method:

"Rather thick, white filter-paper was thoroughly extracted with ether in a Soxhlet apparatus and 5 cc. of the diluted milk (equal to 2 grams of the condensed milk) dropped on a nearly square strip of this paper³ large enough to conveniently soak up the milk. To avoid the formation of candied spots the milk was uniformly spread over the paper by brushing with a small narrow strip of the same kind of paper. After drying in the air the paper was rolled into a loose cylinder and dried in the air-bath at 100° C. for about an hour and a half.

"The fat was then extracted with ether, for two hours, in a Soxhlet apparatus, and a second extraction was made, lasting for an hour to an hour and a half longer. The second extraction usually yielded less than 4 milligrams more of fat, and often none at all. The fat determination was made in duplicate. The greatest difference was 0.2 per cent., usually only a hundredth of a per cent."

In brief, the Adams' method, as applied to sweetened condensed milk, consists in transferring about 2 grams of milk diluted to 5 or 6 cc., to a paper coil of 50-60 sq. in. (100-120 sq. in. of surface, both sides), and extracting the fat by means of ether or petroleum ether.

The quantity of milk taken for the extraction is not a matter

¹ Cornwall: Rep. Dairy Com., N. Y. State, 1890, p. 408; N. J., 1887.

² Wallace: Rep. Dairy Com., N. J., 1899, pp. 43-47.

³ Cornwall: Rep. Dairy Com., N. J., 1891, p. 90; filter-paper of medium thickness 10 × 5 inches. Wiley: Rep. Dairy Com., N. J., 1891; thick filter-paper strips 24 × 24 inches.

of indifference, nor is the solvent, or the method of extraction. Unless the ether is dry and free from alcohol, the coils get too soggy to permit the full extraction of the fat. Even with dry ether or petroleum ether, losses may occur even as high as 0.5 per cent. as against an occasional maximum of about 1 per cent. in a direct extraction. Evidence of this may be obtained by treating the thoroughly exhausted coil after drying, to a thorough soaking in water until all soluble matter is removed, drying the coil, and again exhausting with ether or petroleum ether, when additional fat will be found in the majority of cases.

Direct exhaustion by ether for four hours leaves variable percentages of fat in the residuum on the coils. This is true of other solvents as well. If 2 grams of the condensed milk are used per coil, the coil, after the first exhaustion, which presumably should yield all the fat, should be dried and exhausted with water, again dried and exhausted with the volatile solvent. Forty-nine separate examinations showed differences for the second exhaustion of 0.27 to 1.2 per cent. of which nine ranged from 0.27 to 0.49 per cent.; twenty-three from 0.50 to 0.75 per cent.; and the remainder from 0.75 to 1.2 per cent. That is to say, if the precaution of exhausting the coils with water had not been taken, the fat in the milks would have been underestimated from 0.27 to 1.2 per cent. in actual per cent. of fat by the coil method.

The large variation is due principally to the varying per cent. of cane-sugar in the different samples. As the time of extraction for these varied from two and a half to four hours for the first extraction, a separate set of extractions under fixed conditions was made. The coils (filter-paper strips 22×2.5 inches, were "alcohol-ether" coils, and each coil again exhausted for five hours with the solvent with which it was to be subsequently treated. Simple exhaustion of the coils by ether alone does not remove all the extractable matter from the same. The extractive matter obtained for the eight individual coils varied from 1 milligram to a maximum of 2.5 milligrams. The latter was extracted by petroleum ether from a coil not previously treated with this solvent.

The eight coils were therefore free from extractable matter. Two were taken to be extracted with petroleum ether, and two with a mixture of petroleum ether (15 percent.) and ethyl ether. The first extraction lasted three hours and the second two hours.

After the first three hours' exhaustion, the coils were taken out and dried, and then exhausted with water until all soluble matter was removed. The coils were again dried and again subjected to their respective solvents for two hours. The results obtained were as follows :

PETROLEUM ETHER.

Amount taken. Grams.		Fat. Gram.	Per cent.
2.0355	First extraction.....	0.160	7.86
	Second "	0.013	0.63
			<hr/> 8.49
2.0815	First extraction.....	0.158	7.59
	Second "	0.015	0.72
			<hr/> 8.31 ¹

" ETHER-PETROLEUM " ETHER.

Amount taken. Grams.		Fat. Gram.	Per cent.
2.0645	First extraction.....	0.156	7.55
	Second "	0.017	0.82
			<hr/> 8.37
2.035	First extraction.....	0.1605	7.88
	Second "	0.012	0.58
			<hr/> 8.46

Results by taking about 1 gram of milk and treating as above :

1.0235 grams taken gave 0.0854 gram fat or 8.35 per cent.

1.084 grams taken gave 0.0917 gram fat or 8.46 per cent.

Direct exhaustion with petroleum ether for five hours for the first exhaustion, and two hours further exhaustion after the water treatment, gave :

Amount taken. Grams.		Fat. Gram.	Per cent.
2.0395	First extraction.....	0.159	7.795
	Second "	0.0135	0.661
			<hr/> 8.456
2.013	First extraction.....	0.155	7.699
	Second "	0.0155	0.769
			<hr/> 8.468

The actual time limit will not in all cases do justice to extraction where petroleum ether is used to any extent, as the siphonings are

¹ Water slightly milky, indicating loss of fat.

not always regular. Anhydrous ether, *i. e.*, water-washed ether shaken with concentrated glycerine and redistilled after separation has taken place, shows differences as great as those. The mixture of petroleum ether and ethyl ether was a water-washed ethyl ether mixed with 15 per cent. of petroleum ether prepared by thoroughly shaking and mixing the mixed ether with about 25 per cent. of concentrated glycerine and redistilling the thoroughly separated ether mixture. Coils treated with an anhydrous ether are usually quite crisp when taken out of the extraction apparatus.

Chemists who have made comparative tests have no doubt found that 1 gram of the condensed milk per coil will usually yield all the fat to within 0.2 to 0.3 per cent. on four or five hours' extraction with petroleum ether, or dry ethyl ether, or a mixture of ethyl and petroleum ether, and that the loss rarely exceeds 0.2 per cent.

The amount of milk¹ used per coil is quite a variable one among chemists.

The method of taking a sample and transferring it to the coil may be minor details but important as to possible variation in results by the coil method. While the quantity of original milk will be noticed to vary from 0.5 to 2 grams per coil, it must be apparent that the margin of safety may be overstepped in either direction, for while the maximum quantity may be too large for complete direct extraction, the minimum quantity is too small, as a difference of 1 milligram in fat obtained represents at once 0.2 per cent. For the general run of fat estimation, little fault will be found with results obtained by exhausting the fat from 1 gram of the condensed milk from a *fat-free* coil by the direct exhaustion for four to five hours with petroleum ether, or ether-petroleum ether.

Accuracy in fat estimation to within 0.2 per cent. in sweetened condensed milk is certainly attainable where the necessary precautions are taken. Where 2 grams of the condensed milk are taken the results cannot be depended upon, however, as repre-

¹ T. H. Pearman and C. G. Moor (*Analyst*, 20, 268) use 5 cc. of a 10 per cent. solution; A. H. Allen ("Commercial Organic Analysis," Vol. IV., 2nd ed., p. 235) recommends 5 cc. of a 10 per cent. solution; J. H. Shenstone (*Analyst*, 13, 222) uses 2 grams; Wallace (N. J. State Dairy Com. Rep., 1899, pp. 43-47) uses 2 grams; Cornwall (N. J. State Dairy Com. Rep., 1887, 1890, p. 408) uses 2 grams; H. Throop Richmond and L. K. Boseley (*Analyst*, 18, 170) use 5 cc. of a 15-30 per cent. solution.

senting the full yield of fat, unless the exhausted and dried coil is exhausted with water, and again exhausted with the volatile solvent. Water-washed ether mixed with 10 to 15 per cent. petroleum ether and distilled after shaking out with concentrated glycerine, answers the purpose as well as petroleum ether, as a solvent, and possesses other advantages if the petroleum ether has the proper boiling-point. The commercial petroleum ether is not suitable for this purpose, but suitable fractions of the same may readily be obtained on distillation.

The effective manner in which the cane-sugar prevents the action of the solvents upon the fat is well illustrated in the asbestos-tube method for fat estimation, in which 20 cc. of a 20 per cent. solution of the milk (4 grams) is deposited upon asbestos fiber, and, after drying, exhausted with petroleum ether. This method¹ has been the means of the unjust and unwarranted condemnation of quite a number of condensed milks. It has been proved that the method failed to exhaust all the fat, often 2 to 3 per cent. remaining in the residue, as has been amply demonstrated by exhausting the residue with water and recovering the shortage of fat in the residuum. The asbestos method has found favor in many quarters and was the direct cause of condemnation of pure milks in several instances.

The recurring frequency of unjust condemnation of condensed milk makes it particularly necessary for chemists to exercise great caution in expressing opinions upon whether a milk is skimmed or not. There are instances on record where sweetened condensed milks with high content of cane-sugar and of unquestioned purity were condemned as adulterated on the strength of the analysts finding low percentages of fat (3.8 per cent. lowest and a considerable number ranging from 5.5 to 6.8 per cent.) when more accurate methods demonstrated the presence of over 8 per cent. of fat in all the samples.

A difference of 0.5 per cent. fat has a very important bearing in the enforcement of a law defining the fat contents in milk solids. This is particularly true when the Ritthausen method is used for the estimation of the albuminoids, any error in the fat estimation reflecting its deficiency in increase of the albuminoids (the albuminoids being determined by difference) so that the

¹ Bulletin No. 54, Condensed Milk, Inland Revenue Department, Canada.

ratio between fat and albuminoid is distorted to a degree which would reflect seriously upon the milk under examination, and indicate probable skimming in the minds of some chemists.

This no doubt accounts for the discrepancy in quite a number of published analyses of the excess of albuminoid over fat in what probably were unskimmed milks. When such discrepancies are noticed in an analysis it is advisable to check the results by a nitrogen estimation by the Kjeldahl method, if this was not used in the first instance.

CONCLUSION.

In conclusion I would add that where as much as 2 grams of the sweetened condensed milk is used per "Adams' coil," the full extraction of the fats cannot be depended upon in a direct exhaustion of the coil by a four or five hours' treatment. For general usage 1 gram of milk per *fat-free* coil and four or five hours' exhaustion will give results which will rarely exceed the experimental errors common to complicated methods in which many minor details all must add their perceptible quota to a final result. The asbestos-tube¹ method, without water exhaustion, cannot be considered as giving acceptable results, as the shortage of fat by the same renders the results worthless. Three or four hours' exhaustion of the dried residue with petroleum ether, drying the exhausted mass and reexhausting with petroleum ether, will recover most of the fat.

The details of *modus operandi* especially as to proportion of milk taken to asbestos can no doubt be adjusted so that with the precaution of water exhaustion indicated the results will be fully as reliable as those by other methods. The many factors entering into any method for fat estimation in sweetened condensed milk would indicate that maximum variations of ± 0.1 are possible, and that any method yielding uniform results within that range would be acceptable for all ordinary purposes, as to accuracy.

¹ Bulletin No. 54, Condensed Milk, Inland Rev. Dep't, Canada.

A NEW COAL CALORIMETER.

BY S. W. PARR.

Received July 21, 1900.

IN the study of combustibles and in all tests connected with fuels no data is of any value that does not go back to the thermal units involved. This fact itself is not new but its application, especially in technical work, has had a marked increase in recent years. This increase has come about in spite of, rather than because of, the instruments available for the determination of heat units. It is not necessary here to describe the difficulties and defects connected with existing calorimeters, more than to note perhaps the two extremes; *viz.*, the L. Thompson calorimeter on the one hand which admits of results varying by 15 per cent. from the truth, and the high pressure bomb on the other which, while accurate, requires an elaboration of apparatus and skill in manipulation not conducive to the wide use it deserves.

The calorimeter here described has the advantage of operating without an oxygen gas supply; its manipulation is simple and the extraction of the heat rapid, owing to the compact mass in which the heat is generated. It is especially adapted to soft coal and while designed for technical purposes its factor of error is well within 0.5 per cent., making its results, therefore, easily comparable with those obtained by the Berthelot or Mahler bombs. The principle involved in the process depends upon the liberation of oxygen from such a compound or chemical as shall in turn absorb the products of combustion thereby avoiding the necessity of providing conduits for the gases. A chemical which admirably meets these requirements is sodium peroxide. Its operation may be illustrated by the following experiment which was one of the first used to determine the adaptability of this chemical. A sample of combustible and sodium peroxide in suitable proportion were placed in a short, heavy, copper tube with close-fitting screw plugs at each end and the contents thoroughly mixed by shaking. The bomb was then held in the flame of a Bunsen burner till ignition was effected. Upon cooling and opening it was found that no pressure of gas was pres-

ent and on dissolving out the fused mass the combustion was shown to be complete. The instrument ultimately employed for utilizing these conditions may be best shown by an outline sketch.

A (Fig. 1) is a copper vessel of a little over two liters' capacity insulated by two outer vessels of indurated fiber, B and C, so

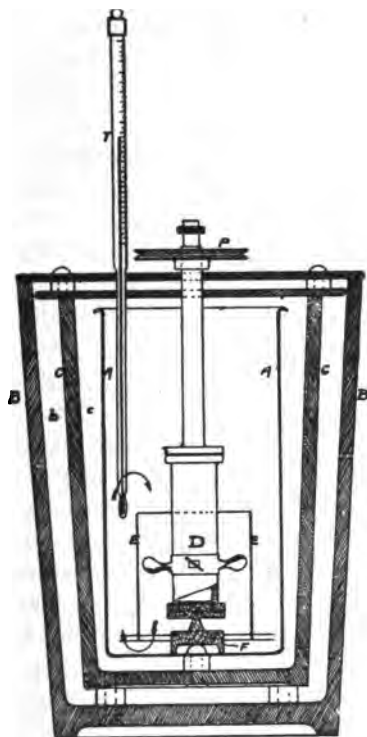


Fig. 1.

placed as to provide further insulation by the air spaces *b* and *c*. The cover is double to correspond with an air space between, the two parts being connected for convenience in handling. The cartridge *D* has an inside capacity of about 25 cc. It rests on a pivot below and extends through the covers above and has a small removable pulley at the end. Turbine wings fastened to spring clips are placed on the cartridge, and a short cylinder *E*, open at both ends, is provided for directing the current set up

by rotation of the vanes attached to the cartridge. The vanes are so set as to deflect the currents downward first along the cartridge and then up along the outside of the cylinder. The stem G of the cartridge is so arranged as to permit the passage of a short piece of No. 12 copper wire (Fig. 2). It is, moreover, pro-



Fig. 2.

vided with a valve D at the lower end which prevents the escape of the enclosed air when heated by the combustion of the charge. The two ends B and C of the cartridge screw on. The process then is as follows: 1 gram of coal ground to pass through a 100-mesh sieve and dried in the oven as usual at 105° – 110° is put into the cartridge, 16 to 18 grams of sodium peroxide are added, the top screwed on and the whole shaken to thoroughly mix the contents. The peroxide varies somewhat in fineness. It should practically all pass through a 25-mesh or 1 mm. sieve. After tapping the cartridge to settle the charge in the bottom, it is placed in the can and 2 liters of water added, the temperature of the water being 3° or 4° lower than the temperature of the work room. The pulley is connected by string to a small water or electrical motor giving about 50 to 100 revolutions per minute to the cartridge. When constant temperature is reached, the reading of the thermometer is taken and the hot wire is dropped through the valve into the charge which is at once ignited and burns completely in two or three seconds. The extraction of the heat is effected in about five minutes. The reading of the maximum temperature is taken and the calculations made as follows:

First.—A correction factor is needed for the hot wire. The average of many determinations on various lengths up to 2 inches establishes a fairly uniform factor of 0.012° C. or 0.021° F. per $\frac{1}{4}$ inch of No. 12 copper wire. In this work the lengths used have been $\frac{1}{4}$ inch and $\frac{3}{8}$ inch and the correction factor for the wire has been 0.006° and 0.009° .

Second.—A correction is made necessary by reason of the heat resulting from the combination of the products of combustion, carbon dioxide and water, with the chemical employed. This

heat of combination causes an excess over and above the actual heat of combustion, amounting to 27 per cent. of the total indicated heat. Hence, this correction must also be applied in the calculation. The method then of calculation will be as follows: Supposing a centigrade scale to have been used, if C' represents the total indicated calories, C the actual calories due to combustion, t the rise in temperature, and w the water employed,

$$\text{then} \quad C' = (t - 0.012^\circ) \times w,$$

$$\text{and} \quad C = C' \frac{C' \times 27}{100},$$

$$\text{or} \quad C = (t - 0.012^\circ) \times w \times 0.73.$$

In case a Fahrenheit thermometer is used the temperature of correction for $\frac{1}{2}$ inch of wire is 0.021° instead of 0.012° and the final result is B. T. U. per pound of coal instead of calories. Of course with a centigrade thermometer the ultimate reading is changed from calories to B. T. U. by multiplying the calories obtained by 1.8.

A word of explanation is necessary as to the method of arriving at the factor for the heat of absorption of the products of combustion. The two elements concerned are carbon and hydrogen. For the carbon dioxide resulting from the combustion of the former, the correction factor is easily determined. Pure sugar carbon is prepared and run in the calorimeter as above described. The average of a number of such determinations gave a total calorific result of 11,084. Now taking as the accepted figure for the heat of combustion of carbon in calories, 8,080, we have therefore an increase of 3,004 calories due to the heat of absorption of the carbon dioxide by the chemical. By computation this is found to be 27.1 per cent. of the total indicated heat. Now as to the heat due to the absorption of water from the combustion of hydrogen the problem is not so simple. The burning of sugar affords no indication, for seemingly other compounds than water are formed and as in the case of sugar burned in the bomb calorimeter, while the results are constant and repeat themselves with exactness, they vary so widely from the theoretical data as to make it evident that the combinations do not proceed in a simple manner. Naphthalene does not afford a factor, chiefly owing to its volatility and consequent

faulty combustion. The liberation of a known weight of water in the interior of the cartridge gave very indifferent results, the water not disseminating throughout the peroxide but incrusting itself in a moist mass. Many other methods were tried with the result that so far at least it has been necessary to fall back on empirical data obtained from burning widely different varieties of coals and checking the same coals by combustion in standard bomb calorimeters. The following table gives the results thus obtained, using coals varying in their ash content from 3 to 32 per cent., and in water from 1 to 14 per cent. Also as wide a variation in the character of their hydrocarbons as possible, using a cannel coal,—Pennsylvania gas coal, a lignite and soft coals from widely separated districts in Illinois. Supposing the factor for absorption of water formed from a given weight of hydrogen to be approximately the same per cent. of total heat evolved as in the case of carbon dioxide, *viz.*, 27 per cent. and applying this factor throughout, we have the following results obtained by running parallel combustions in a standard Atwater or Mahler bomb calorimeter and the sodium peroxide apparatus. In a number of samples the process was conducted in both the Atwater and Mahler bombs. The instruments, however, checked so closely that this practice was not continued throughout the tests. The proximate analysis is included in the table in order that the wide variations in the character of the coals may be indicated (see table).

A few facts should be noted :

(a) It has been discovered after most tedious experience that a comparison of calorimeters should be made at approximately the same time. For example a series of calorific determinations made on finely ground samples on May 12, 1900, were found to give a reading 2.4 per cent. less on July 12, 1900. It was necessary to repeat practically all the above determinations on this account, all results showing a slow deterioration in the finely ground samples. This subject will receive further attention later.

(b) In the table it should be noted that the first five samples are from the same mine and vary but slightly in composition. The particular purpose in introducing this series was to note if

Kind of coal.	Proximate analysis.				B. T. U. per pound air-dried coal.			
	Moisture.	Volatiles combustible.	Fixed carbon.	Ash.	Sulphur.	Bomb calorimeter.	New method.	Variation from standard bomb in per cent.
216 Cartersville, Ill., mine run.....	4.87	34.11	52.17	8.85	0.85	12,205	12,214	+0.07
217 " " washed No. 1.....	4.66	33.99	54.21	7.14	0.74	12,289	12,286	0.00
218 " " " 2.....	4.31	35.12	55.01	5.56	0.87	12,914	12,934	+0.08
220 " " " 4.....	4.86	33.26	55.29	6.59	1.15	12,355	12,345	-0.08
221 " " dust from washer.....	5.50	32.97	53.01	8.52	1.16	12,384	12,336	-0.39
226 Odin, Ill., pea coal.....	7.27	35.76	42.96	14.01	3.89	11,025	11,064	+0.35
227 Farmington, Ill., mine run.....	11.22	35.93	36.60	16.25	3.98	9,986	10,018	+0.32
228 Pennsylvania gas coal.....	0.92	36.66	58.94	3.46	1.40	14,270	14,275	0.00
229 Kentucky cannel coal.....	0.99	32.33	34.35	32.33	1.07	10,313	10,328	+0.14
230 Mississippi lignite.....	14.56	43.82	29.30	12.32	...	8,316	8,378	+0.74

the calorimeter would differentiate between such small variations in the inert material, the ash and water.

Tabulating the results with reference to these inert materials and giving simply the calorimetric reading for each we have :

No.	Total of water and ash.		B. T. U.
	Per cent.		
216	13.79		12,214
217	11.80		12,286
218	9.87		12,924
220	11.45		12,345
221	14.02		12,056

(c) It has already been mentioned but attention should again be called to the fact that with the calorimeter it is necessary to operate on the oven-dried sample for the reason that the water, if left in the sample, gives off heat in combining with the chemical; hence, a gram sample is weighed and dried in the oven or if the per cent. of moisture is known, an oven-dried sample may be weighed out, making allowance for the water. No other conditions vary the results. About 17 times the weight of coal is the best amount of peroxide to insure complete combustion but variations from 16 to 20 times the amount do not appreciably vary the results. Indeed with careful work and a good thermometer the instrument repeats its own results fully as closely as the bomb calorimeters. The usual practice, moreover, has been to work with half-gram samples, using a measured quantity,—8 to 9 grams of peroxide. With a suitable room and reasonable precautions as to temperature of both room and water employed, exceedingly constant and satisfactory results may be obtained which should vary less than 0.5 per cent. from the best figure obtainable with a standard instrument.

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URBANA, ILL.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 28.]

ON THE DETERMINATION OF PHOSPHORIC ACID AS PHOSPHOMOLYBDIC ANHYDRIDE.

BY H. C. SHERMAN AND HENRY ST. JOHN HYDE.

Received July 23, 1900.

ALTHOUGH a great amount of work has been done in this country upon the subject of phosphorus determination, practically no attention seems to have been given to methods

which involve the ignition of ammonium phosphomolybdate and weighing of the residue. A given weight of phosphoric acid yields about sixteen times as much phosphomolybdic anhydride as magnesium pyrophosphate, and the "yellow precipitate can be ignited much more quickly and apparently with quite as definite results as it can be dried. It seems strange, therefore, that less attention has been given to this than to the other rapid gravimetric methods.

The first attempt to determine phosphoric acid as phosphomolybdic anhydride was probably that of Meineke.¹ The phosphate was precipitated by means of the ordinary acid molybdate reagent from a solution containing 20 to 25 per cent. of ammonium nitrate, heated to 50°–60° and vigorously stirred. After washing with a weakly acid solution of ammonium nitrate, the precipitate was heated below redness for fifteen minutes. The residue was believed to be of constant composition and to it was assigned the formula $P_2O_5 \cdot Mo_2O_6$.

Hanamann² about ten years later published a method very similar to that of Meineke but recommended that the precipitation be made at room temperature.

Later Meineke³ made an extended series of determinations on solutions of pure phosphates from the average of which he calculated the percentage of P_2O_5 in the residue to be 3.949 per cent., agreeing well with the formula, $P_2O_5 \cdot 24MoO_3$. He recommended that in the presence of a little iron the precipitation be carried out at 50° in the presence of 5 per cent. of ammonium nitrate, using the ordinary acid molybdate solution while if the solution contained much iron at least 10 per cent. of ammonium nitrate and 5 to 10 per cent. of strong nitric acid should be present and the precipitation carried out at a higher temperature. Good results are reported on two samples of phosphate.

Woy⁴ developed the following method and applied it to a variety of technical products:

Reagents.—(1) A 3 per cent. solution of ammonium molybdate; (2) ammonium nitrate solution—340 grams per liter; (3) nitric acid of 1.153 sp. gr.; (4) wash solution containing

¹ *Repert. anal. Chem.*, 8, 153 (1885); *Ztschr. anal. Chem.*, 26, 636 (1887).

² *Chem. Ztg.*, 19, 553 (1895).

³ *Ibid.*, 20, 108 (1896).

⁴ *Ibid.*, 21, 441 and 469 (1897).

200 grams ammonium nitrate and 160 cc. of nitric acid in 4 liters of water.

Procedure.—To an aliquot part of the solution corresponding to 0.5 gram substance, add 30 cc. ammonium nitrate solution and 10 to 20 cc. of the nitric acid and heat until bubbles commence to rise, then add the necessary quantity of molybdate solution heated to the same degree (about 80° in our experiments). The reagent is run into the middle of the solution which is kept in motion during the operation. After fifteen minutes when the precipitate has settled, the solution is decanted through a porcelain Gooch crucible, the precipitate washed by decantation with 50 cc. of the wash solution and then dissolved in the beaker in dilute ammonia and reprecipitated by adding hot nitric acid, drop by drop, stirring or shaking the solution. Filter on the porcelain Gooch crucible and wash with the hot wash solution. Finally place the porcelain crucible inside of a nickel crucible and heat until the bottom of the latter is dull red. After fifteen minutes the precipitate is transformed into $P_2O_5, 24MoO_3$.

Pellet¹ considers the second precipitation of ammonium phosphomolybdate recommended by Woy to be unnecessary. Having seen only a brief abstract of his paper we do not know the nature of the experiments on which his conclusion is based.

Hanamann² suggests that contamination with silica is best avoided by carrying out the precipitation at a low temperature and in the presence of considerable free nitric acid.

Some preliminary trials with microcosmic salt solutions having given results quite favorable to Woy's method whether with or without a second precipitation, we were led to compare on a number of samples: (1) The well-known molybdate-magnesia method carried out according to the directions of the Association of Official Agricultural Chemists and here called the official method; (2) Woy's method as published; (3) Woy's method, omitting the second precipitation of ammonium phosphomolybdate. The samples tested were not only "mixed" fertilizers but nearly all of them were "composites" so that together they represent a large variety of fertilizer materials.

¹ *Rev. Chim. Analyt. Appl.*, v. (20), 405; *Abs. Analyst*, 23, 25 (1898).

² *Ztschr. landw. Vers-Sta. Unt.*, 3, 53; *Abs. J. Soc. Chem. Ind.*, 378 (1900).

In each case solution was effected by boiling with 30 to 50 cc. of concentrated nitric acid and 5 to 10 cc. concentrated hydrochloric acid. The organic matter was not burned off before the solution nor was the silica removed by evaporation. The results obtained are shown in Table A which follows :

TABLE A. RESULTS WITH AND WITHOUT REPRECIPITATION.

No.	Description of sample.	Official method. Per cent. P_2O_5 .	Woy's method	
			as published. Per cent. P_2O_5 .	omitting 2nd precipitation. Per cent. P_2O_5 .
1.	Mixed fertilizer 11.16	11.13	11.16
2.	" " 12.23	12.26	12.27
3.	" " 12.95	12.84	13.02
4.	" " 11.15	11.26	11.11
5.	" " 9.80	9.73	9.60
6.	" " 10.84	10.95	10.93
7.	" " 10.53	10.62	10.70
Average		11.24	11.26	11.26

In these samples the second precipitation demanded by Woy's method seems to have been entirely unnecessary. We therefore tried the effects of salts of a few of the commoner acids and bases upon the results obtained by ignition of the first yellow precipitate. A commercial superphosphate was dissolved as above and its phosphoric acid content determined by the official method and by ignition of the first "yellow" precipitate. To aliquot parts of the same solution, corresponding to 0.4 gram of substance, were added the various salts, about 0.4 gram being used in each case. The yellow precipitate was ignited without reprecipitation. The determinations were not duplicated as in no case was the deviation from the true percentage greater than might easily be due to manipulation of a new method. The results are shown in Table B.

TABLE B. EFFECTS OF IMPURITIES.

Sample.	Method.	Per cent. P_2O_5 .	Average.
Superphosphate.	Official method.	18.26
"	Ignition of first yellow ppt.	18.14	18.20
" + $NaNO_3$	" "	18.16
" + KNO_3	" "	18.10
" + $Sr(NO_3)_2$	" "	18.31
" + $Mg(NO_3)_2$	" "	18.21
" + $Fe(NO_3)_3$	" "	18.15
" + $Ba(NO_3)_2$	" "	18.33
" + $(NH_4)_2SO_4$	" "	18.17
" + NH_4Cl	" "	18.10	18.19

¹ Woy found that very large quantities of ammonium chloride interfered with the precipitation of ammonium phosphomolybdate.

In carrying out the method it was naturally found that the precipitate formed was more granular and more easily washed if the molybdate solution was added very slowly and with vigorous stirring. The modification which follows seems to us to combine most of the best features of Woy's and Gladding's methods.

MODIFIED METHOD.

To the solution representing 0.2 to 0.5 gram of the sample, add 25 cc. strong ammonia (sp. gr. 0.90), neutralize with nitric acid and then add 5 to 8 cc., according to the impurities present, of concentrated nitric acid (sp. gr. 1.42) in excess. Bring the solution to a bulk of about 150 cc. and a temperature of 50° C. and maintain at this temperature (conveniently by standing the beaker in a pan of warm water) while adding, drop by drop with constant stirring, a neutral 3 per cent. solution of ammonium molybdate sufficient to give an excess of about 20 cc. Stir vigorously and allow to stand for about ten minutes; decant through a porcelain Gooch crucible and wash the precipitate three times by decantation with 50 to 70 cc. and then on the filter with 200 to 250 cc. of a cold solution of one part concentrated nitric acid in 100 parts of water. Finally the precipitate is ignited as described by Woy, leaving a residue of $P_2O_5.24MoO_3$.

Suction was employed in the filtration, and in washing on the filter the precipitate was well stirred up with the dilute acid wash solution. The neutral ammonium molybdate solution was employed simply to permit of the direct addition of the desired amount of nitric acid irrespective of the amount of the molybdate solution to be used.

As would be expected in working any new method, a few individual determinations were found on repetition to be wrong. These "wild" results were too high, doubtless from the precipitation of impurities, and emphasize the necessity of careful, slow addition of the molybdate solution. Only one sample was encountered in which the results obtained by the method described differed by more than two-tenths of one per cent. from those given by the official method. This was a phosphatic slag which contained, according to the official method, 17.27 per

cent. and according to the new method 16.97 per cent. of P_2O_5 . The final precipitate obtained by the official method was, however, contaminated with iron and this result was thus undoubtedly too high, that by the new method being probably nearer the truth. These results on this sample are therefore omitted from the table which follows.

Table C below shows the results obtained by Woy's method, omitting the second precipitation, and by the modified method described above, together with the results obtained by the official method. The samples are numbered in the order in which they were analyzed.

TABLE C. COMPARISON OF RESULTS.

No.	Description of sample.	Per cent. P_2O_5 found.		
		Official method.	Woy's method, omitting the second precipitation.	Modification of Woy's method, page 66.
1.	Mixed fertilizer	11.16	11.16
2.	"	12.23	12.27
3.	"	12.95	13.02
4.	"	11.15	11.11
5.	"	9.80	9.60
6.	"	10.84	10.93
7.	"	10.53	10.70
8.	Acid phosphate.....	18.26	18.14
9.	Mixed fertilizer	14.90	14.91
10.	"	11.21	11.27
11.	"	13.75	13.66
12.	"	11.44	11.54	11.45
13.	"	17.55	17.57	17.42
14.	Steamed raw bone.....	32.34	32.32
15.	Natural soft phosphate	20.80	20.92
16.	South Carolina phosphate....	27.60	27.74
17.	Florida phosphate.....	29.76	29.76
18.	South Carolina phosphate....	27.92	27.80
19.	Basic slag phosphate	17.77	17.67
	Average, Nos. 1 to 13	12.75	12.76
	Average, Nos. 12 to 19	23.15	23.14

CONCLUSION.

In all of the twenty samples examined, which represent a large

variety of the common phosphatic materials of the fertilizer industry, the determination of phosphoric acid as phosphomolybdic anhydride was found to give satisfactory results even without a reprecipitation of the ammonium phosphomolybdate.

The presence in considerable quantity of some of the common acids and bases was found to be without appreciable effect.

With either modification of the method the average result obtained on all the samples analyzed was practically the same as that yielded by the official method which would seem to indicate that such variations as occur are due mainly to manipulation.

By the method described a determination may be completed in much less time than by any other gravimetric method with which we are familiar but in handling several samples simultaneously, the saving of time is less apparent.

COLUMBIA UNIVERSITY, NEW YORK CITY, July, 1900.

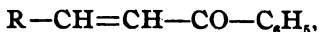
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

THE ACTION OF SODIUM ALCOHOLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

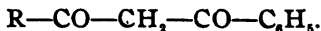
BY F. J. POND AND ARTHUR S. SHOFFSTALL.

Received August 1, 1900.

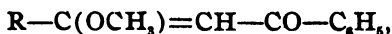
In a preceding communication¹ on this subject it was mentioned that sodium methylate reacts with the dibromides of certain unsaturated ketones of the general formula,



yielding 1,3-diketones of the formula,



Thus benzylidene acetophenone dibromide was readily converted into *dibenzoyl methane*, and anisylidene acetophenone dibromide was found to give a 1,3-diketone analogous to dibenzoyl methane, and called *anisoyl benzoyl methane*. It was suggested that the formation of these diketones from the dibromides of unsaturated ketones was accomplished by the production of unsaturated ethers,

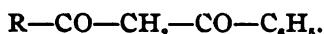


¹ Pond, Maxwell, and Norman: This Journal, 21, 955.

which were converted by hydrolysis with dilute acids into the unsaturated ketone alcohols,

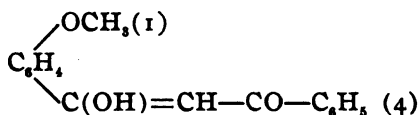


and these, in turn, by an intramolecular change into the saturated 1,3-diketones,

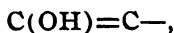


Such a reaction would be somewhat analogous with the formation of ketones from the dibromides of anethol, isosafrol, and other propenyl compounds.

Closer investigation of the compound obtained from anisylidene acetophenone dibromide and of its derivatives leads us to believe that the last-mentioned change of the unsaturated ketone alcohol into the saturated diketone does not take place, and that the compound is a keto-enolic modification of anisoyl benzoyl methane and may be called *α-oxyanisylidene acetophenone*,



Its solution in alcohol is colored an intense brownish red by the addition of ferric chloride; aqueous ferric acetate, made by mixing the solutions of one part of ferric chloride and three parts of sodium acetate, throws out the ferric salt of *α-oxyanisylidene acetophenone* as a brick-red, crystalline precipitate, which is insoluble in water and alcohol, but soluble in dilute hydrochloric acid. W. Wislicenus¹ has suggested that the formation of such colored iron compounds on the addition of ferric chloride to the alcoholic solutions is a property of compounds containing the group,



such as phenols and the enolic modifications of *β*-keto-compounds; also, that in these colored iron compounds the metal is joined to the oxygen atom, a view which Claisen² also holds regarding the constitution of the iron salts of the *β*- or 1,3-diketones.

This compound is soluble in dilute alkalies, and is reprecipitated by acids. A green, crystalline copper salt is precipitated from its alcoholic solution by an alcoholic solution of copper ace-

¹ W. Wislicenus: *Ann. Chem. (Liebig)*, 291, 174.

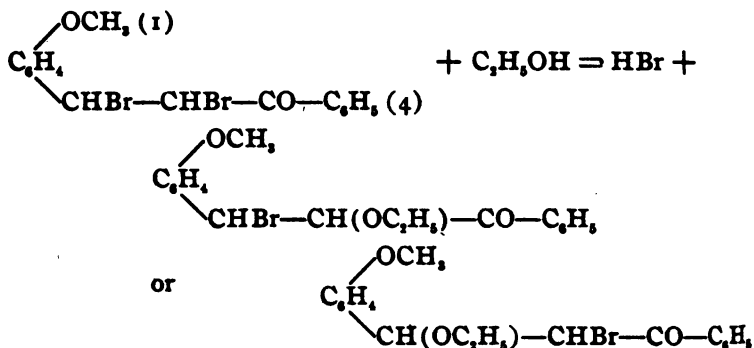
² L. Claisen: *Ibid.*, 281, 344.

tate. It decolorizes immediately a solution of potassium permanganate in the cold, but it does not yield an additive product with bromine. It is indifferent towards acetic anhydride and benzoyl chloride.

The experimental part of our work is preceded by the following brief review of the contents of this paper.

The method of preparation of anisylidene acetophenone, the starting-point of our investigation, is slightly modified, by means of which a larger yield of the compound, melting at 78° , is obtained. This substance unites readily with two atoms of bromine, forming an additive product. The dibromide can not be recrystallized unchanged from alcohol, but it separates without change from acetic ether in large crystals, melting at 139° to 140° .

When anisylidene acetophenone dibromide is dissolved in alcohol and the solution is boiled for a short time, hydrogen bromide is eliminated and an alcohol addition-product of monobromo-anisylidene acetophenone is produced :

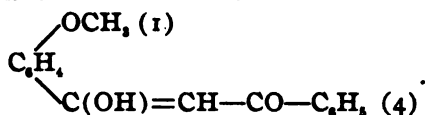


This is a saturated compound, which melts at 73.5° to 74.5° . When heated carefully in a distilling flask, no change is to be noted until the temperature reaches about 155° to 160° ; a clear liquid then comes over having the odor and boiling-point of ethyl alcohol, and yielding the iodoform reaction. If the distillation be interrupted as soon as alcohol ceases to be given off, the liquid remaining in the flask solidifies and crystallizes from alcohol or ethyl acetate in large plates, melting at 94.5° ; these are shown to be monobromoanisylidene acetophenone.

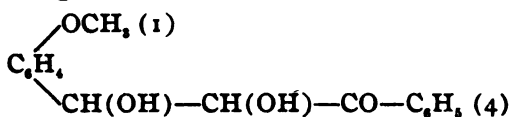
The analogous methyl alcohol addition-product was prepared,

and crystallized from methyl alcohol in fine crystals, which melt at 102° . The propyl alcohol addition-product is an oil, and is not further examined.

In a previous paper¹ it was shown that when anisylidene acetophenone dibromide was heated with two molecules of sodium methylate or ethylate and the resultant product hydrolyzed with hydrochloric acid, a compound was formed which melted at 131° to 132° ; this compound was called anisoyl benzoyl methane. Further investigation has shown that it consists of α -oxyanisylidene acetophenone, *i. e.*, it is the α - or acid-modification of the diketone, $C_{16}H_{14}O_3$, and is to be represented by the formula,

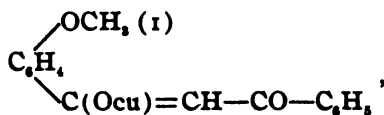


The filtrate obtained in the preparation of this compound yields an exceedingly small quantity of a silky, crystalline substance, which melts at 90° and is exceptionally soluble in alcohol; the analysis of this compound indicates that it has the composition represented by the formula, $C_{18}H_{16}O_4$. It may possibly prove to be the keto-glycol,



Until a method of preparation is found by which a suitable quantity of this substance can be obtained and further experimental evidence is secured, we do not care to commit ourselves regarding its structure. Should further investigation prove it to be the keto-glycol suggested above, its study will lead to very interesting results.

α -Oxyanisylidene acetophenone yields quantitatively a copper salt,²



which melts with decomposition at 247° to 249° . α -Oxyanisylidene

¹ *Loc. cit.*

² Cu = $\frac{1}{2}$ atom Cu.

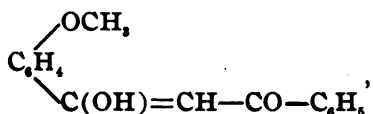
dene acetophenone is easily regenerated in a pure condition by warming this copper salt with dilute hydrochloric acid.

The action of hydroxylamine hydrochloride upon an alcoholic solution of α -oxyanisylidene acetophenone gives α,γ -methoxyphenyl-phenyl-isoxazole, melting at 120° ; it crystallizes from alcohol in small flakes, which possess a brilliant mother-of-pearl luster. Claisen¹ has shown that monoximes of the β - or 1,3-diketones are not generally known. In attempts to prepare them, water usually splits off and an intramolecular anhydride formation takes place, giving the isoxazoles. J. Wislicenus² succeeded in preparing a monoxime from α -benzylidene acetophenone by the action of free hydroxylamine; but it showed a great tendency to lose water with the formation of α,γ -diphenyl-isoxazole.

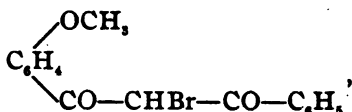
An isomeric methoxyphenyl-phenyl-isoxazole is formed by the action of an excess of potassium hydroxide upon the mixed alcoholic solutions of anisylidene acetophenone dibromide and hydroxylamine hydrochloride. It crystallizes from alcohol in small, silky needles, which melt at 128° .

Acetic anhydride and benzoyl chloride do not react with the hydroxyl group of α -oxyanisylidene acetophenone.

Bromine seems to convert α -oxyanisylidene acetophenone into a bromine derivative of the β -modification of the diketone. Instead of absorbing two atoms of bromine and yielding an additive product as would naturally be anticipated by the formula,



an atom of bromine is substituted for one hydrogen atom, and the compound,



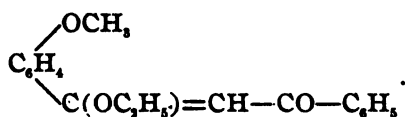
anisoyl benzoyl monobromomethane, is formed. It crystallizes well, and melts at 127.5° to 128.5° . It gives no coloration with ferric chloride and alcohol, and does not form a copper salt by

¹ L. Claisen : *Ber. d. chem. Ges.*, 24, 3906; 21, 2178; 24, 390; 25, 1787.

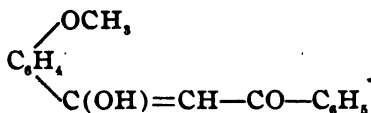
² J. Wislicenus : *Ann. Chem. (Liebig)*, 308, 250.

the addition of an alcoholic solution of copper acetate. It apparently contains no hydroxyl group.

An important part of our work is to determine, if possible, the exact course of the reaction by which the enolic-ketone is formed from anisylidene acetophenone dibromide by the action of sodium alcoholate. When one molecule of the dibromide is boiled with two molecules of sodium ethylate, the resulting product consists of an unsaturated ether,

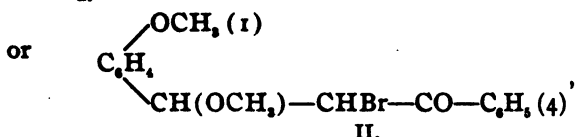
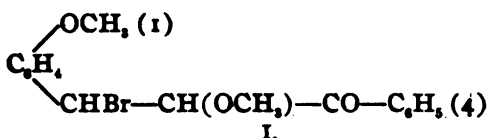


Dilute acids hydrolyze this compound with the formation of ethyl alcohol and the keto-enol,

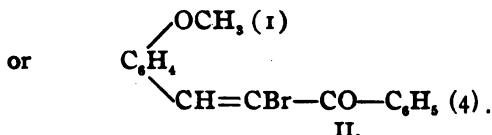
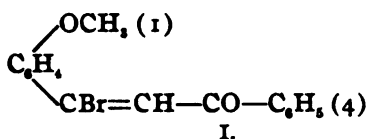


When sodium methylate is employed, the unsaturated methyl ether is produced, which also yields α -oxyanisylidene acetophenone on hydrolysis. The sodium alcoholate seemed to have a double action in that it split off one bromine atom as hydrogen bromide and then replaced the second bromine atom with the methoxyl or ethoxyl group. It therefore remained to determine whether the sodium alcoholate could react under certain conditions so that the two phases of the reaction could be separated, and the intermediate products isolated.

For this purpose we treated one molecule of the dibromide with a dilute solution of one molecule of sodium methylate in methyl alcohol. The product consists of two compounds: the one crystallizing in small needles and melting at 101.5° to 102.5° is the methyl alcohol addition-product of monobromoanisylidene acetophenone, and is formed in small quantity; the other is monobromoanisylidene acetophenone, which crystallizes in beautiful plates and melts at 94° . On heating the methyl alcohol additive compound it loses methylalcohol and yields monobromoanisylidene acetophenone. This alcohol addition-product should probably be represented by one of the two following structural formulas,

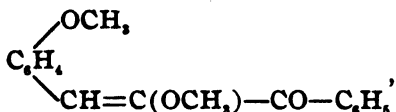


and monobromoanisylidene acetophenone by the formula,

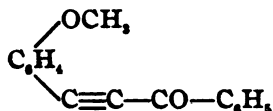


For the present we prefer the formula I. for each compound for the following reasons:

If the alcohol addition-product has the structure as represented by formula II, the unsaturated monobromide resulting from it by the elimination of methyl alcohol must have the formula II, thus containing the bromine atom in the β -position to the methoxyphenyl group. It would be expected that by the action of another molecule of sodium methylate upon this compound, a new ether,

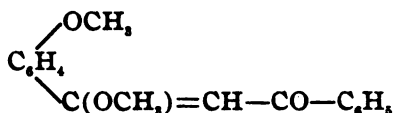


would be formed by the replacement of the bromine atom by methoxyl, or the monobromide might lose hydrogen bromide and yield a compound containing a triple linkage, benzoyl methoxyphenyl acetylene,



Neither of these compounds, however, have been obtained.

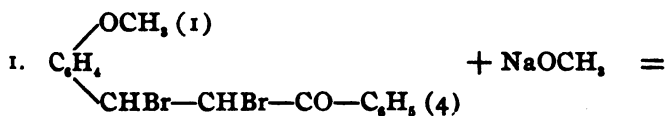
If the alcohol addition-product be represented by formula I, then by the splitting off of alcohol an unsaturated bromide having the above formula I with the bromine atom in the α -position would result. Such a compound might react with one molecule of sodium methylate giving rise to the same unsaturated methyl ether,

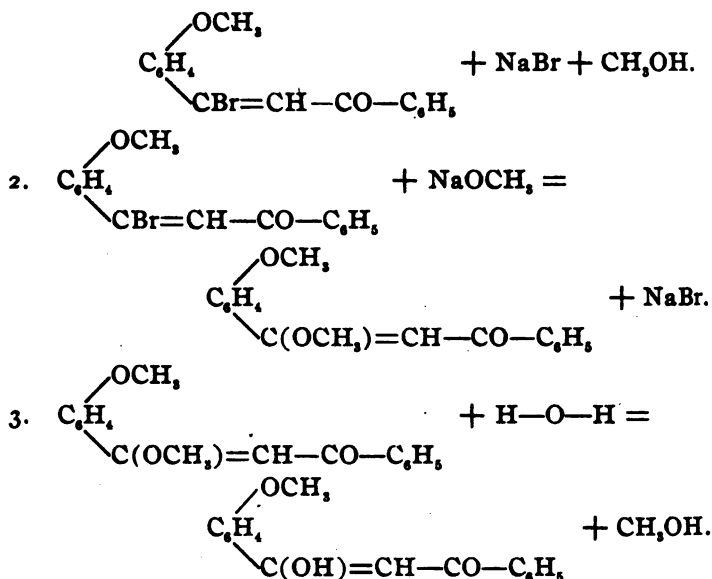


which is produced by the treatment of the dibromide with two molecules of sodium methylate, and by the hydrolysis of this ether the same keto-enole must result. Our experiments show that the reaction takes place in this manner, since the monobromide does react with sodium methylate, yielding the same ether which results by the action of an excess of methylate upon the dibromide, and from which α -oxyanisylidene acetophenone is formed by hydrolysis.

The formation of α -monobromoanisylidene acetophenone and of its alcohol addition-product in the same reaction would seem to indicate that one molecule of sodium alcoholate eliminates hydrogen bromide from a large part of the dibromide, yielding the unsaturated monobromide, and at the same time it replaces one atom of bromine in another smaller portion of the dibromide with the methoxyl group. It is also possible that, under the conditions of the experiment in which great care must be taken to avoid any excess over one molecule of sodium methylate, in order to prevent the elimination of both bromine atoms, that all of the sodium methylate is employed to remove hydrobromic acid, and that the small quantity of the methyl alcohol addition-product is due simply to the action of the methyl alcohol on some unchanged dibromide.

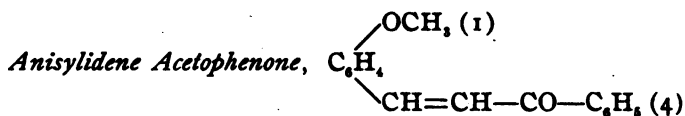
α -Oxyanisylidene acetophenone is probably formed by the action of sodium alcoholate upon anisylidene acetophenone dibromide in accordance with the following equations:





In the first phase of the reaction, the bromine atom in the β -position to the methoxyphenyl group is eliminated as hydrogen bromide with the formation of an unsaturated monobromide, while in the second stage, the bromine atom in the α -position is replaced by the methoxyl group, giving an unsaturated ether, which is readily hydrolyzed into the enolic ketone.

EXPERIMENTAL.



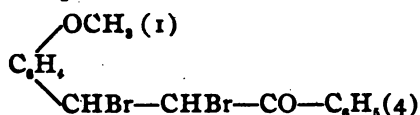
This substance is very readily prepared by the following method: Twelve grams of acetophenone and 13.6 grams of anisaldehyde (molecular proportions) are dissolved in 50 cc. of alcohol and treated with 5 cc. of a 20 per cent. solution of sodium methylate. After standing for about fifteen minutes, the solution is shaken vigorously for a few minutes, when the product separates as a yellow, crystalline solid; this is filtered by the pump, washed sparingly with cold alcohol, dried, and recrystallized from alcohol. It crystallizes from alcohol in long, light yellow

needles, and melts at 77° to 78° . It is easily soluble in hot ethyl and methyl alcohols, ether, and chloroform. Upon analysis it gave the following results :

- I. 0.1582 gram gave 0.4674 gram carbon dioxide and 0.0822 gram water.
 II. 0.1603 gram gave 0.4733 gram carbon dioxide and 0.0846 gram water.

	Calculated for $C_{10}H_{14}O_2$	I.	Found.	II.
Carbon.....	80.65	80.58		80.53
Hydrogen.....	5.88	5.77		5.86

Anisylidene Acetophenone Dibromide,

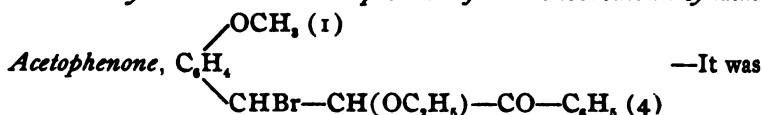


Twenty-five grams of anisylidene acetophenone were dissolved in 125 cc. of ether and the solution was cooled ; 16.8 grams (one molecule) of bromine were added slowly and with constant shaking. After two-thirds of the bromine had been introduced, the product began to separate in fine, white crystals. The crystalline precipitate was filtered, washed well with cold ether to remove any slight excess of bromine, and dried on a porous plate. It was crystallized from ethyl acetate and obtained in thick prisms, melting with decomposition at 139° to 140° . It can not be recrystallized unchanged from ethyl or methyl alcohol ; when dissolved in either of these solvents, hydrogen bromide is given off and crystalline compounds are formed, which will be subsequently described. It is readily soluble in acetic ether and crystallizes from it without evolution of hydrobromic acid ; it is only sparingly soluble in ether:

It was analyzed with the following results :

- I. 0.1807 gram gave 0.3228 gram carbon dioxide and 0.0567 gram water..
 II. 0.1708 gram gave 0.3024 gram carbon dioxide and 0.0543 gram water.
 III. 0.1669 gram gave 0.1566 gram silver bromide.
 IV. 0.1825 gram gave 0.1738 gram silver bromide.

	Calculated for $C_{10}H_{14}O_2Br_2$	I.	II.	Found.	III.	IV.
Carbon	48.24	48.72	48.28	
Hydrogen	3.52	3.49	3.53	
Bromine.....	40.20	39.93		40.52

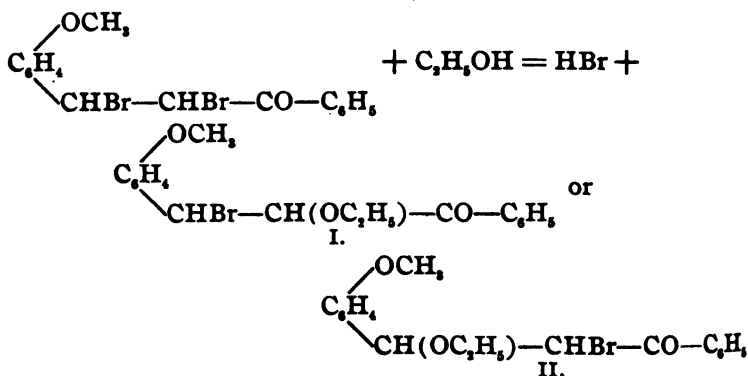
The Ethyl Alcohol Addition-product of α -Monobromoanisylidene

noticed that when the preceding compound was crystallized from alcohol, considerable hydrogen bromide was given off and the resultant compound was quite different from the original dibromide. Fifty grams of anisylidene acetophenone dibromide were crystallized from ethyl alcohol and the resulting crystals were repeatedly recrystallized until they showed the constant melting-point, 74° to 75° . It is deposited from alcohol in long, white needles. It is unaltered by crystallization from methyl alcohol and by boiling its solution in methyl alcohol for several hours. It was dried *in vacuo*, and analyzed with the following results:

- I. 0.1832 gram gave 0.4017 gram carbon dioxide and 0.0877 gram water.
 II. 0.1822 gram gave 0.3969 gram carbon dioxide and 0.0872 gram water.
 III. 0.1871 gram gave 0.0970 gram silver bromide.
 IV. 0.1671 gram gave 0.0870 gram silver bromide.

	Calculated for $\text{C}_{18}\text{H}_{15}\text{O}_2\text{Br}$.	Calculated for $\text{C}_{18}\text{H}_{19}\text{O}_2\text{Br}$.	I.	II.	Found.	III.	IV.
Carbon	60.56	59.50	59.80	59.41
Hydrogen ...	4.10	5.23	5.32	5.32
Bromine	25.23	22.04	22.06	22.15	

The analysis indicated that the compound was not the monobromoanisylidene acetophenone, $\text{C}_{18}\text{H}_{15}\text{O}_2\text{Br}$, at first anticipated, but that it was the ethyl alcohol addition-product of this bromide. It probably results from anisylidene acetophenone dibromide according to the following equation:



For the reasons suggested in the introduction we prefer formula I.

The substance behaves like a saturated compound. When it is dissolved in carbon tetrachloride it absorbs no bromine; the first drop of bromine added gives it a permanent red color, hydrogen bromide being evolved, and when one molecular proportion of bromine is added and the solvent evaporated, a crystalline substitution-product results.

The following experiment also indicates that it is an alcohol addition-product of α -monobromoanisylidene acetophenone.

Twenty-five grams of the substance (m. p. 74°) were heated in a distilling flask. It melted to a clear liquid which gradually assumed a yellowish color. At about 161° bubbles began to form and rise from the bottom of the flask, and a clear liquid distilled over. The temperature was further increased very slowly to 175° , when the distillation was interrupted. Two and one-half grams of liquid distillate were obtained having the odor of ethyl alcohol, and boiling at 77° to 78° ; it yielded iodoform on treatment with iodine and potassium hydroxide, and was thus identified as alcohol. The yellow oil remaining in the flask was poured into a beaker, when it solidified at once, and was recrystallized from acetic ether; it separated in large plates, melting at 94.5° , and was proved to be α -bromoanisylidene acetophenone.

The same addition-product results on boiling the dibromide with alcohol in a reflux apparatus for several hours. Thus, 25 grams of anisylidene acetophenone dibromide were boiled with 200 cc. of alcohol on the water-bath for several hours, and the contents then allowed to crystallize. On recrystallization from alcohol, the product separated in long, white needles, which melted at 73.5° to 74.5° , and gave the following on analysis:

- I. 0.1963 gram gave 0.1004 gram silver bromide.
- II. 0.1230 gram gave 0.1187 gram silver bromide.

	Calculated for $C_{12}H_{10}O_2Br$.	I.	Found.	II.
Bromine	22.04	21.76		21.95

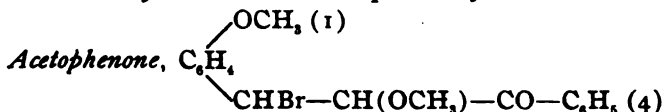
An attempt to prepare monobromoanisylidene acetophenone by boiling an alcoholic solution of the dibromide with a molecular proportion of potassium acetate resulted in the formation of

the alcohol addition-product. Twenty-five grams of anisylidene acetophenone dibromide were dissolved in 200 cc. of alcohol and treated with an alcoholic solution of 6.2 grams of potassium acetate; after boiling for three hours, the resulting potassium bromide was filtered off at once. On cooling, a compound separated from the clear filtrate in long, white needles; these were recrystallized from alcohol, and melted at 73.5° to 74.5° . Analysis showed it to be the ethyl alcohol addition-product:

- I. 0.2055 gram gave 0.1076 gram silver bromide.
 II. 0.2008 gram gave 0.1044 gram silver bromide.

	Calculated for $C_{18}H_{18}O_2Br$.	I.	Found.	II.
Bromine	22.04	22.23		22.12

The Methyl Alcohol Addition-product of α -Monobromoanisylidene



It was to be expected that a compound analogous to the preceding one would result on crystallizing the dibromide from methyl alcohol. Accordingly, 20 grams of anisylidene acetophenone dibromide were dissolved in hot methyl alcohol, the solution boiled for a few minutes and then allowed to crystallize. Hydrobromic acid fumes were given off during the boiling of the solution and continuously during the cooling. The resulting crystalline compound was repeatedly crystallized from methyl alcohol and obtained in the form of small, white needles, melting sharply at 102° . The compound is fairly soluble in methyl alcohol, and very soluble in acetic ether; it is also readily soluble in ethyl alcohol, and crystallizes from it, without change, in small needles, melting at 102° .

Analyses of the product recrystallized from methyl alcohol and dried *in vacuo* gave the following:

- I. 0.1819 gram gave 0.3905 gram carbon dioxide and 0.0800 gram water.
 II. 0.1818 gram gave 0.3887 gram carbon dioxide and 0.0800 gram water.
 III. 0.2022 gram gave 0.1073 gram silver bromide.
 IV. 0.1961 gram gave 0.1048 gram silver bromide.

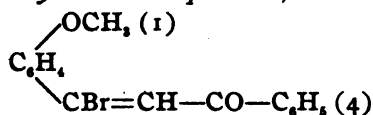
	Calculated for $C_{17}H_{17}O_2Br$.	I.	II.	Found.	III.	IV.
Carbon	58.45	58.55	58.31	
Hydrogen	4.87	4.89	4.89	
Bromine	22.92	22.58		22.74

This compound is the methyl alcohol addition-product expected. In attempting to distil it under diminished pressure, it suffered complete decomposition. When 25 grams were heated at the ordinary pressure, the substance melted to a clear liquid and, on raising the temperature to 160° , bubbles began to rise; from 167° to 180° a small quantity of a clear distillate was obtained, while the liquid in the flask had assumed a yellowish color. At 180° the heat was removed, and, on cooling, the contents of the flask solidified at once; this solid was crystallized from ethyl acetate and obtained in large, slightly yellow-colored plates, melting at 94° , thus showing it to be α -monobromoanisylidene acetophenone.

Anisylidene acetophenone dibromide dissolves in propyl alcohol with evolution of hydrogen bromide; on evaporation of the solvent, a colorless oil results, but it was not examined.

THE ACTION OF ONE MOLECULE OF SODIUM METHYLATE UPON
ANISYLIDENE ACETOPHENONE DIBROMIDE.

α -Monobromoanisylidene Acetophenone,



To a solution of sodium methylate, made by dissolving 1.5 grams of sodium in 125 cc. of methyl alcohol, was added 25 grams of the dibromide. The dibromide dissolved at once, forming a light yellow colored solution. After boiling for one hour, a small quantity of sodium bromide had separated and the solution was no longer alkaline to litmus. The sodium bromide was separated by filtration and the filtrate allowed to evaporate slowly. A product began to separate in large, yellow plates, and, after standing for some time, it was removed and the mother-liquor allowed to evaporate to dryness, when a second product, more soluble in alcohol than the plates, was obtained. The yellow plates were washed with water, pressed on a porous plate, and crystallized from acetic ether. The resulting crystals were again rubbed on a plate to remove oily impurities, and recrystallized first from alcohol and then acetic ether. The pure product separates from acetic ether in large, beautiful plates, which

are nearly colorless, and melt at 94.5° . Its composition is shown by the analysis:

- I. 0.1816 gram gave 0.4001 gram carbon dioxide and 0.0676 gram water.
- II. 0.1873 gram gave 0.4125 gram carbon dioxide and 0.0680 gram water.
- III. 0.1938 gram gave 0.1161 gram silver bromide.
- IV. 0.1898 gram gave 0.1130 gram silver bromide.

	Calculated for $C_{10}H_{10}O_2Br$.	I.	Found. II.	III.	IV.
Carbon	60.56	60.09	60.06
Hydrogen	4.10	4.13	4.03
Bromine	25.23	25.49	25.33

This compound is, therefore, monobromoanisylidene acetophenone, and apparently constitutes the chief product of this reaction.

The second product, which is obtained by the evaporation to dryness of the methyl alcoholic filtrate as above mentioned, was pressed on a plate, since it contained some oil. It was then dissolved in acetic ether; plates of monobromoanisylidene acetophenone separated at first, and when the ether had nearly all evaporated, the second product was deposited in fine, white needles. A complete separation of the two compounds was made by fractional crystallization from acetic ether and then alcohol. The second product was purified by crystallization from alcohol, from which it was deposited in small, white needles, melting at 101.5° to 102.5° .

Analysis gave the following:

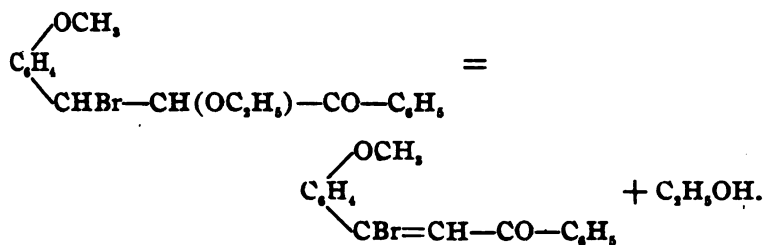
- I. 0.1805 gram gave 0.3859 gram carbon dioxide and 0.0800 gram water.
- II. 0.1808 gram gave 0.3874 gram carbon dioxide and 0.0825 gram water.
- III. 0.2096 gram gave 0.1114 gram silver bromide.
- IV. 0.2068 gram gave 0.1110 gram silver bromide.

	Calculated for $C_{11}H_{11}O_2Br$.	I.	Found. II.	III.	IV.
Carbon	58.45	58.31	58.44
Hydrogen	4.87	4.92	5.07
Bromine	22.92	22.62	22.84

This substance is, therefore, the methyl alcohol addition-product of α -monobromoanisylidene acetophenone.

The α -monobromide is also readily formed by the action of one molecule of sodium ethylate on the dibromide. It is, however, best prepared by carefully heating the ethyl or methyl al-

cohol addition-products until the alcohol is removed, as was mentioned in the consideration of these compounds. It is purified by crystallizing from alcohol and then ethyl acetate, and forms large, well-defined plates, which melt at 94° . Its formation by the decomposition of the alcohol addition-products on heating may be represented as follows:



THE ACTION OF TWO MOLECULES OF SODIUM METHYLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

Fifty grams of the dibromide were added to a solution of sodium methylate, made by the action of 7.5 grams of metallic sodium on 150 cc. of methyl alcohol. After heating the mixture for a short time on the water-bath, a reaction took place, the liquid became dark colored, and sodium bromide was deposited; the mixture was boiled for about one hour. On completion of the reaction, the sodium bromide was dissolved by adding 200 cc. of water, a dark colored oil, heavier than water, being thrown out. Twenty cc. of concentrated hydrochloric acid¹ were introduced, rendering the liquid acid and changing its color from brown to light yellow; it was then boiled for one-half hour, or until the oil was completely converted into a light yellow solid. After cooling, this was filtered off and the filtrate allowed to stand for several days, when another compound separated in very fine, white needles; this will be described in a subsequent part of this paper. The solid was washed well with water, dried, and crystallized from alcohol, in which it is spar-

¹ In other experiments it was determined that dilute sulphuric acid and even acetic acid also affect the conversion of the oil into the solid, giving identically the same product as concentrated hydrochloric acid. Carbon dioxide, however, does not affect this transformation.

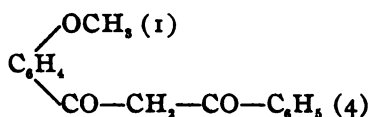
ingly soluble; it separated in fine, white crystals, melting at 130° to 131° .

The analysis gave the following:

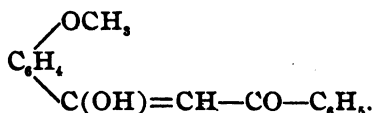
- I. 0.2003 gram gave 0.5498 gram carbon dioxide and 0.1018 gram water.
 II. 0.1981 gram gave 0.5424 gram carbon dioxide and 0.1001 gram water.

	Calculated for $C_{16}H_{14}O_2$.	Found.	
		I.	II.
Carbon.....	75.59	74.86	74.67
Hydrogen.....	5.51	5.65	5.61

This compound was first obtained by G. M. Norman and was previously described¹ as the 1,3-diketone, anisoyl benzoyl methane,



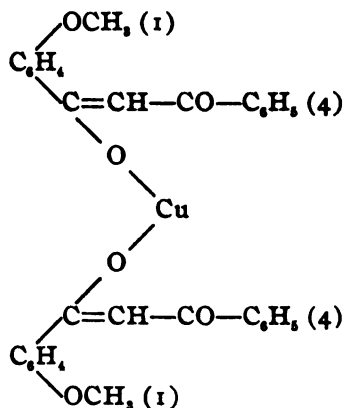
Its alcoholic solution is colored a deep violet-red with ferric chloride, and it is soluble in the hydroxides of potassium and sodium. Closer investigation, however, leads us to believe that this compound consists wholly, or at least for the most part, of the unsaturated ketone alcohol, α -oxyanisylidene acetophenone,



J. Wislicenus² obtained a mixture of α -oxybenzylidene acetophenone and dibenzoyl methane by the treatment of benzylidene acetophenone dibromide with an alcoholic solution of potassium hydroxide, and he found that the two substances could be readily and completely separated by the action of an alcoholic solution of copper acetate; the keto-enolic modification gave an insoluble copper salt, while the other remained unchanged in the alcoholic solution. This method of treatment with alcoholic copper acetate was applied to the above-mentioned substance (m. p. 130° to 131°) with the result that it was completely converted into a copper salt.

¹ Pond, Maxwell, and Norman: This Journal, 21, 966.

² J. Wislicenus: Ann. Chem. (Liebig), 308, 241.

Copper Salt of α -Oxyanisylidene Acetophenone,

The substance is formed when an alcoholic solution of the preceding compound is treated with alcoholic copper acetate. An alcoholic solution of 3 grams of copper acetate is added slowly and with vigorous agitation to the hot, alcoholic solution of 5 grams of the above compound (m. p. 130° to 131°). A fine, green precipitate of the copper salt separates almost immediately. The liquid above the precipitate remains colorless or slightly yellow until an excess of copper acetate is added, when it becomes green. It is essential that the liquid be kept near the boiling-point during the operation, otherwise the original compound separates. The precipitate is filtered and washed with alcohol until no trace of copper acetate is observed; it is further washed with water, then alcohol, and finally ether. It is insoluble in water, alcohol, ether, and carbon disulphide; very sparingly soluble in chloroform and benzene, and separates from the latter solvent in exceedingly small needles.

When the precipitated substance is purified by repeated washing with water, alcohol, and ether, it melts with decomposition at 247° to 249° . The analysis of such a preparation yielded the following figures:

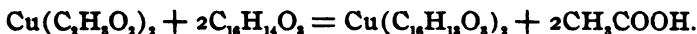
I. 0.1984 gram gave 0.4868 gram carbon dioxide, 0.0832 gram water, and 0.0282 gram copper oxide.

II. 0.2386 gram gave 0.5850 gram carbon dioxide, 0.0955 gram water, and 0.0334 gram copper oxide.

III. 0.1825 gram gave 0.0257 gram copper oxide.

	Calculated for $C_{22}H_{20}O_9Cu$.	I.	Found. II.	III.
Carbon	67.41	66.92	66.86
Hydrogen	4.56	4.66	4.45
Copper	11.16	11.36	11.18	11.25

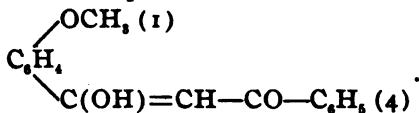
The formation of this copper salt is, therefore, represented by the following equation :



It consists of small, light green needles. It burns with a very smoky flame, leaving a residue of cupric oxide. Hot, dilute sulphuric acid decomposes it only very slowly, while hot, dilute hydrochloric acid readily converts it into cupric chloride and α -oxyanisylidene acetophenone; this reaction forms an excellent method of obtaining the latter compound in a pure condition.

The alcohol was distilled off from the combined green filtrate of the copper salt and the wash alcohol, and the residue extracted with ether. The excess of copper acetate was filtered, the ethereal solution dried, and the ether evaporated in a vacuum over calcium chloride. The residue consisted of a small amount of a dark, thick oil, which did not solidify after standing for two months, and decomposed on distillation under diminished pressure. No definite compound could be obtained from it.

α -Oxyanisylidene Acetophenone,



This compound was easily regenerated by boiling the copper salt for a short time with hydrochloric acid (1 : 3), and crystallizing the product from alcohol. It separates in small, yellowish white needles, melting at 130° to 131° , and boils at 284° to 286° under 44 mm. pressure, the distillate solidifying at once to an almost white, crystalline mass. The substance, purified by distillation and subsequent crystallization from alcohol, gave the following results on analysis :

- I. 0.3009 gram gave 0.8309 gram carbon dioxide and 0.1501 gram water.
 II. 0.2516 gram gave 0.6959 gram carbon dioxide and 0.1268 gram water.

	Calculated for $C_{18}H_{14}O_3$.	I.	Found. II.
Carbon	75.59	75.31	75.43
Hydrogen	5.51	5.54	5.60

It decomposes on distillation under atmospheric pressure. It is almost insoluble in cold alcohol, soluble in hot alcohol. It is easily soluble in chloroform, benzene, ethyl acetate, and carbon disulphide. Its alcoholic solution is colored a deep violet-red by ferric chloride, while ferric acetate precipitates the neutral iron salt of the keto-enole as a brick-red, crystalline substance, insoluble in alcohol and water. It readily forms the copper salt when treated with copper acetate and alcohol. Dilute nitric acid oxidizes it, forming a mixture of acids, probably benzoic and anisic. It dissolves in sodium and potassium hydroxide solutions and is reprecipitated with acids, melting at 129° to 130° . When the solution of the alkali is fairly concentrated and hot, the compound suffers decomposition into anisic acid, melting at 182° to 183° , and a ketone having an odor similar to that of acetophenone.

The Compound, $C_{16}H_{16}O_4$.—The filtrate obtained in the preparation of the crude α -oxyanisylidene acetophenone by the action of two molecules of sodium methylate upon anisylidene acetophenone dibromide was allowed to stand; after twenty-four hours, a white, silky, crystalline substance separated. After two weeks, when no further separation of crystals was observed, it was filtered, pressed carefully on a plate to remove oily impurities and repeatedly crystallized from alcohol. It is exceedingly soluble in alcohol, and it was found best in crystallizing to make a concentrated solution and then to place the dish in a freezing-mixture, when the compound is deposited in very fine, silky needles, melting at 90° . Its alcoholic solution is neither colored by ferric chloride nor precipitated by copper acetate. Its solution in benzene removes the color of a permanganate solution very slowly.

This substance is formed in an extremely small quantity. The analysis gave values required for $C_{16}H_{16}O_4$.

I. 0.1573 gram gave 0.4082 gram carbon dioxide and 0.0865 gram water.

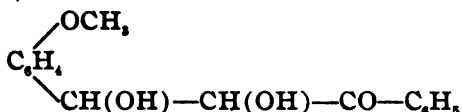
II. 0.1441 gram gave 0.3736 gram carbon dioxide and 0.0794 gram water:

	Calculated for $C_{16}H_{16}O_4$.	I.	Found.	II.
Carbon.....	70.59	70.77		70.70
Hydrogen.....	5.88	6.11		6.12

When one gram of the compound was boiled with an excess

of acetic anhydride for two hours, and the product poured into cold water, a thick, yellow oil separated. We were unable to isolate a definite compound from the oil.

Until a method of preparation is discovered by which a larger yield of this compound may be obtained, no satisfactory conclusions can be arrived at regarding its constitution. The analysis indicates the formula, $C_{16}H_{18}O_4$, and from its method of formation it is possible that the compound may prove to be the ketone glycol,



Owing to the want of material and limited time, the investigation of this substance was interrupted; the study of it will, however, be continued during the year.

THE ACTION OF SODIUM ETHYLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

The following experiments indicate that the product of the action of two molecules of sodium ethylate or methylate on the dibromide consists of the ethyl or methyl ether of α -oxyanisylidene acetophenone, which, on the addition of hydrochloric, sulphuric, or acetic acid, is converted into the corresponding alcohol and α -oxyanisylidene acetophenone.

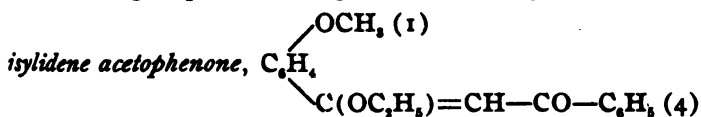
Twenty-five grams of the dibromide were added to a slight excess over two molecules of sodium ethylate (4 grams of sodium in 100 cc. of ethyl alcohol), and heated for about two hours on the water-bath. All of the alcohol was then distilled off, water was added, and the solution rendered neutral to litmus by a few drops of acetic acid; the heavy oil, which separated, was taken up with ether, the ethereal solution washed repeatedly with water, dried with anhydrous sodium sulphate, and the ether distilled off. The residue consisted of a light red colored oil.

On standing, this oil is changed, crystals being gradually deposited, and, in the course of two or three weeks, a large part of the oil is converted into a crystalline mass. This change is accelerated by the addition of acids, and, indeed, strong hydrochloric acid causes the conversion to take place in a few seconds, dilute sulphuric and acetic acids reacting more slowly. The

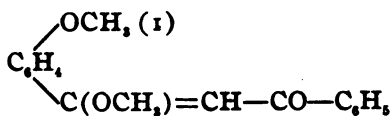
solid is identified in each case as α -oxyanisylidene acetophenone.

This transformation of the oil into a solid is caused by the oil being readily hydrolyzed by the acids with the splitting off of alcohol and the formation of α -oxyanisylidene acetophenone, as is shown by the following: About 15 grams of freshly prepared oil were treated in the cold with 10 cc. of dilute hydrochloric acid (1 part acid to 1 of water); the oil solidified almost immediately, with a great evolution of heat. Twenty-five cc. of water were added, the solid was filtered, and the presence of ethyl alcohol in the filtrate was easily and distinctly recognized by the iodoform test. The solid crystallized from alcohol and melted at 128.5° ; it gave the reaction with ferric chloride and copper acetate, and was identified as α -oxyanisylidene acetophenone.

The elimination of alcohol and the production of this solid indicates, without doubt, that the substance obtained by the action of two molecules of sodium ethylate on the dibromide contains an ethoxyl group, and we regard it as the *ethyl ether of α -oxyan-*



When the dibromide is treated with 2 molecules of sodium methylate, in the same manner as above, an oil is obtained which remains unchanged for several weeks when kept in a tightly closed flask. On standing in an open flask, it is very gradually converted into a crystalline solid. When the oil is acted upon by dilute hydrochloric acid in the cold, it is quickly changed into a solid, with considerable elevation of the temperature. The solid is brittle and slightly yellow in color; it crystallizes from alcohol in small needles, melting at 129° , and is α -oxyanisylidene acetophenone. Although the oil could not be secured in a suitable condition for the analysis, it is exceedingly probable that the substance is to be regarded as the *methyl ether of α -oxyanisylidene acetophenone*,



The reaction of 2 molecules of sodium alcoholate upon anisylidene acetophenone dibromide appears to consist in first splitting off 1 molecule of hydrobromic acid with the formation of the unsaturated compound, α -bromoanisylidene acetophenone, and then in replacing the bromine atom in this compound with methoxyl or ethoxyl. The resulting unsaturated ether is readily hydrolyzed by acids with the production of α -oxyanisylidene acetophenone.

THE ACTION OF SODIUM METHYLATE ON THE ADDITION-PRODUCT OF α -MONOBROMOANISYLI-DENE ACETOPHENONE AND ETHYL ALCOHOL.

Twenty-five grams of the addition-product were treated in the usual manner with 1 molecule of sodium methylate (2 grams of sodium in 100 cc. of methyl alcohol). On the completion of the reaction, 150 cc. of water were introduced, a dark colored oil being thrown out; hydrochloric acid was added until the liquid gave an acid reaction, and the mixture heated on the water-bath for a short time. The oil was rapidly converted into a solid, which was filtered and crystallized from alcohol; it melted at 129° , gave the color reaction with ferric chloride and alcohol, and a green precipitate with alcoholic copper acetate. It is α -oxyanisylidene acetophenone.

After standing during twenty-four hours, a small quantity of the compound, $C_{16}H_{16}O_4$, was deposited in long, slender needles from the filtrate obtained above; it melted at 89° .

THE ACTION OF SODIUM METHYLATE ON α -MONOBROMOANISYLI-DENE ACETOPHENONE.

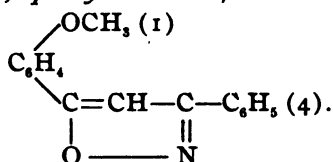
Fifteen grams of the monobromide were added to a solution of 1 molecule of methylate in methyl alcohol (1 gram of sodium in 75 cc. of methyl alcohol). After boiling for half an hour, the resultant sodium bromide was dissolved by the addition of water, the solution rendered strongly acid with acetic acid and heated for thirty minutes. On cooling, a crystalline substance separated, was filtered, and recrystallized from alcohol. It melts at 129.5° , reacts with ferric chloride and copper acetate, and is α -oxyanisylidene acetophenone. The yield of the enolic ketone was very good. A small quantity of the compound, $C_{16}H_{16}O_4$, melting at 89° , was deposited from the filtrate.

α-Oxyanisylidene Acetophenone and Acetic Anhydride.—Ten grams of *α*-oxyanisylidene acetophenone were boiled with 25 grams of acetic anhydride for eight hours, and the mixture then allowed to stand for forty-eight hours. On pouring the product into ice-water, a red oil, heavier than water, was produced; this was separated, washed with water, and allowed to stand. Since it did not become solid, it was taken up in alcohol, from which a substance crystallized in yellowish white needles similar to the original compound. It melted at 130° to 131°, reacted with ferric chloride and copper acetate, and appeared to be unchanged *α*-oxyanisylidene acetophenone. The acetate could not be isolated.

No better success was attained on treatment with benzoyl chloride, as in every case the unchanged material was obtained.

ACTION OF HYDROXYLAMINE HYDROCHLORIDE UPON *α*-OXYANISYLIDENE ACETOPHENONE.

α-Methoxyphenyl-phenyl-isoxazole,



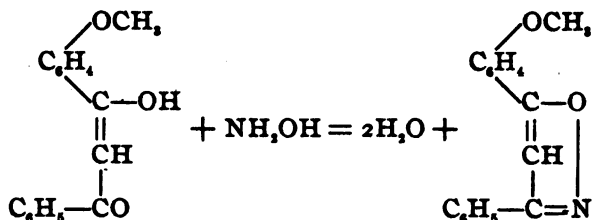
Five grams of *α*-oxyanisylidene acetophenone were dissolved in just enough hot alcohol to effect a solution in a small flask with reflux apparatus; 4 grams (3 molecules) of hydroxylamine hydrochloride were added, and the mixture was boiled gently during four hours. On cooling, a substance crystallized in beautiful, white crystals, resembling somewhat those of sulphocarbanilide. It was filtered, washed with water, dried, and crystallized from alcohol; it separated from this solvent in colorless, shining leaflets, which melted sharply at 119° to 120°. The following numbers were obtained upon analysis:

- I. 0.1502 gram gave 0.4199 gram carbon dioxide and 0.0722 gram water.
- II. 0.1935 gram gave 0.5422 gram carbon dioxide and 0.0914 gram water.
- III. 0.7050 gram gave 39.2 cc. nitrogen at 23° and 726 mm.
- IV. 0.6945 gram gave 39.4 cc. nitrogen at 24° and 726 mm.

	Calculated for $C_{16}H_{15}O_3N$.	I.	II.	Found.	III.	IV.
Carbon	76.49	76.24	76.42
Hydrogen	5.18	5.34	5.25
Nitrogen	5.37	5.97	6.06

This compound is insoluble in water, alkali solutions, and dilute acids, difficultly soluble in cold alcohol, more readily soluble in hot alcohol and carbon disulphide, and very easily soluble in chloroform, ether, benzene, and ethyl acetate. Ferric chloride and copper acetate do not react with its alcoholic solution. It appears to be a very stable substance. It remains unaltered by boiling with a solution of potassium hydroxide. Concentrated hydrochloric acid dissolves it very sparingly, but is without further action upon it.

It is, without doubt, an isoxazole derivative, and results from the reaction of hydroxylamine upon α -oxyanisylidene acetophenone according to the equation,



It is probably analogous to the isoxazoles obtained by Claisen¹ by the action of hydroxylamine on the 1,3-diketones. J. Wislicenus² also obtained $\alpha\gamma$ -diphenyl-isoxazole, melting at 140.5° to 141° , by the action of hydroxylamine hydrochloride on α -oxybenzylidene acetophenone. Goldschmidt³ had previously produced a diphenyl-isoxazole, melting at 141° , by the reaction of an excess of sodium hydroxide on the mixed, warm, alcoholic solutions of benzylidene acetophenone dichloride and hydroxylamine hydrochloride.

It was, therefore, of interest to determine whether the isoxazole above described or an isomeric compound would be formed by the treatment of anisylidene acetophenone dibromide with

¹ L. Claisen: *Ber. d. chem. Ges.*, 24, 3006.

² J. Wislicenus: *Ann. Chem. (Liebig)*, 308, 249.

³ Goldschmidt: *Ber. d. chem. Ges.*, 28, 2540.

hydroxylamine hydrochloride and an excess of potassium hydroxide.

Isomeric Methoxyphenyl-phenyl-isoxazole, $C_{18}H_{15}O_2N$.—Twenty grams of anisylidene acetophenone dibromide are dissolved in 200 cc. of alcohol; to this is added a solution of 7 grams (2 molecules) of hydroxylamine hydrochloride in 10 cc. of water, and the mixture is heated to the boiling-point; 17 grams of potassium hydroxide in 20 cc. of water are then added very gradually, and with constant shaking, to the hot solution. A very vigorous reaction takes place with elimination of potassium salts, the solution assuming a yellowish red color. After standing for about ten minutes, the inorganic salts are filtered off, and on cooling the filtrate, a product separates in very fine, white needles. These are filtered, washed well with water, dried, and recrystallized from alcohol. It is deposited in very slender, silky needles, which melt at 127° to 128° .

The yield is further increased by precipitating the first alcoholic filtrate with water.

The analysis gave the following results :

- I. 0.1887 gram gave 0.5282 gram carbon dioxide and 0.0894 gram water.
- II. 0.1693 gram gave 0.4737 gram carbon dioxide and 0.0837 gram water.
- III. 0.6972 gram gave 39.2 cc. nitrogen at 25° and 728 mm.

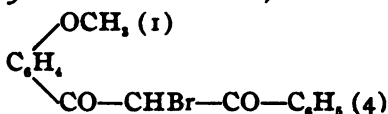
	Calculated for $C_{18}H_{15}O_2N$.	I.	Found. II.	III.
Carbon	76.49	76.34	76.31
Hydrogen	5.18	5.26	5.49
Nitrogen	5.57	6.00

This compound is soluble in alcohol, ether, carbon disulphide, and readily soluble in chloroform, benzene, and acetic ether. It dissolves, to a slight extent, in hot, concentrated hydrochloric acid, and is reprecipitated on the addition of water; cold, concentrated sulphuric acid dissolves it quite easily with almost no development of color, and when the solution is poured into water, the substance is thrown out apparently unaltered. Boiling potassium hydroxide solution is without action on the substance, and ferric chloride gives no coloration with its alcoholic solution, and copper acetate no precipitate.

This compound, melting at 127° to 128° , is probably isomeric

with the preceding isoxazole, melting at 119° to 126° , although its constitution is not yet definitely determined.¹

Anisoyl Benzoyl Monobromomethane,



When α -oxyanisylidene acetophenone is dissolved in ether or chloroform and treated with one molecular proportion of bromine, hydrobromic acid is given off with gradual decoloration. On the evaporation of the solvent, a crystalline residue is obtained, which separates from alcohol in brilliant, white crystals, melting at 128° .

The analysis gave results corresponding to the formula, $\text{C}_{18}\text{H}_{15}\text{O}_3\text{Br}$.

- I. 0.1784 gram gave 0.3790 gram carbon dioxide and 0.0655 gram water.
- II. 0.1792 gram gave 0.3787 gram carbon dioxide and 0.0643 gram water.
- III. 0.2062 gram gave 0.1158 gram silver bromide.
- IV. 0.2060 gram gave 0.1166 gram silver bromide.

	Calculated for $\text{C}_{18}\text{H}_{15}\text{O}_3\text{Br}$.	I.	II.	Found.	III.	IV.
Carbon	57.66	57.94	57.64
Hydrogen	3.90	4.08	3.99
Bromine	24.02	23.89	24.08

It is soluble in alcohol, carbon disulphide, and ether; readily soluble in chloroform, benzene, and acetic ether.

Its alcoholic solution is not colored by ferric chloride, and gives no precipitate with copper acetate. It is probable, therefore, that the compound contains no hydroxyl group, and it may

¹ In an investigation which is being carried on in this laboratory, Mr. H. J. York has obtained the α -diphenyl-isoxazole described by J. Wislicenus (*Ann. Chem.* (Liebig), 308, 249) by the treatment of α -oxybenzylidene acetophenone (resulting by the action of two molecules of sodium alcoholate upon benzylidene acetophenone dibromide and subsequent hydrolysis of the unsaturated ether with hydrochloric or acetic acid) with hydroxylamine hydrochloride. It crystallizes from hot alcohol in thick, colorless tablets, and melts at 141° to 142° . On treating benzylidene acetophenone dibromide in alcoholic solution with hydroxylamine hydrochloride and an excess of potassium hydroxide in a manner similar to the above, a compound resulted which was deposited from alcohol in thin, lustrous leaflets; these melted sharply at 140° . This compound contains nitrogen and is apparently identical with the substance described by Goldschmidt (*Ber. d. chem. Ges.*, 28, 2540) as diphenyl-isoxazole. Although at the present time it is not proved that these two isoxazoles are different, the indications are that they are isomeric and not identical, and that they are analogous to the isoxazoles obtained from α -oxyanisylidene acetophenone and from anisylidene acetophenone dibromide.

be regarded as a bromine derivative of the neutral or β -modification of the diketone, anisoyl benzoyl methane.

We expect to continue this work in various directions, and to extend the investigations to other analogously constituted compounds.

A NEW VOLUMETRIC METHOD FOR THE ESTIMATION OF COPPER.

BY S. W. PARR.

Received August 13, 1900.

EXPERIMENTS looking to the use of the thiocyanates in volumetric processes have been carried on in this laboratory for over two years past. While the results obtained are in many ways very satisfactory, it is intended here to make note of one application, which gives results of great practical value.

The iodine and cyanide methods for the estimation of copper are far from satisfactory. Two methods, recently proposed in this Journal,¹ making use of the precipitation of copper as cuprous thiocyanate, mark a decided advance in methods. It is believed that the process here outlined has further points of advantage. It involves the precipitation of the copper as cuprous thiocyanate, the oxidation of the copper without decomposition of the alkali thiocyanate and the titration of the acidified thiocyanate with standard permanganate. In practice the two latter steps are one operation, but one filtration is necessary and for most ores thirty to forty minutes are ample for a determination from the time of weighing the sample to the time of the final titration.

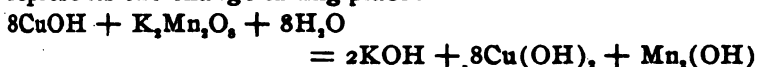
Some attention must be given to the condition of the solution before precipitating the copper as cuprous thiocyanate. If the solution contains free sulphuric acid it should not exceed 1 or 2 per cent. in amount. Stronger solutions on heating with thiocyanate have a tendency to liberate free sulphur which remains with the precipitate and in the final reading gives variable results. The same thing is true regarding hydrochloric acid. With nitric acid no free sulphur is liberated. Here, however, an excess of acid prevents the reduction and complete pre-

¹ This Journal, 19, 940 (1899) and 20, 610 (1900).

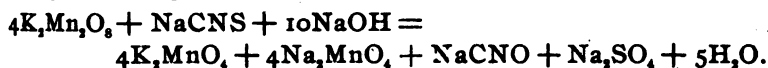
precipitation of the copper, so that in any case an amount of free acid in excess of 1 or 2 per cent. is to be avoided. Since the greatest safety seems to reside with the nitric acid it is preferred. This is an advantage also for in the initial treatment of mattes, ores, etc., it avoids the necessity of evaporating the solution to sulphuric acid fumes for the removal of the nitric acid. Further it may be noted that a small amount of sulphuric acid, resulting from the action of strong nitric acid or otherwise present, does not interfere with the precipitation. The reduction of the copper is best effected by a strong solution of sulphur dioxide, a few cc. being added from time to time. A 10 per cent. solution of sodium sulphite may be similarly used but it is better not to add acid to such a solution to liberate the sulphurous acid but allow it to be liberated by the free acid of the copper solution. The next point to be observed is the addition of the alkaline thiocyanate. The precipitated cuprous thiocyanate is very appreciably soluble in an excess of this reagent. Two cc. of a 10 per cent. solution of potassium thiocyanate will precipitate several times the amount of copper that could be conveniently handled in the subsequent titration; hence, that amount of reagent is sufficient to use, and at the same time there is no danger of re-solution of the precipitate. This reagent may be added with the reducing agent, before or after it, seemingly without preference. Heating on a water-bath or hot plate with stirring should be continued till the separation of the precipitate is complete and the supernatant liquid becomes perfectly clear. This requires from five to ten minutes.

The filtration is best made on a thick asbestos felt well packed in a $1\frac{1}{4}$ -inch porcelain filter funnel using a pump. A felt $\frac{1}{4}$ inch or more thick should be used. The washing which should be made with hot water is complete when the filtrate, upon acidifying, will not decolorize a drop of permanganate. Special care should be taken that none of the precipitate passes through with the filtrate. The filter with the asbestos-pulp is returned to the beaker, 2 or 3 cc. of caustic soda (10 per cent.) solution are added, well stirred and warmed to 60° or 70° . The mixture after a few minutes is ready for titrating with the standard permanganate, the object being first to add to the alkaline mixture the amount of permanganate needed to oxidize the

cuprous hydroxide formed from the addition of the alkali, then to acidify and proceed with the rest of the titration to oxidize the thiocyanic acid. The first part of the reaction, that which takes place in the alkaline condition, is confined to the copper so long as any cuprous hydroxide remains. The following equation represents the change taking place:



Now it is not necessary that at the exact end of this reaction on the copper the change should be made to the acid condition, but it is necessary that this point be fully passed in order that upon acidifying there may not be reprecipitated some cuprous thiocyanate. Fortunately it is easy to tell when this point has been passed, and in this way, when the copper has been all oxidized there begins a reaction between the alkaline thiocyanate and the permanganate which results in the formation of the green manganate thus:



It will be seen, therefore, that the bright yellow of the cuprous hydroxide becomes more and more mixed with the dark brown of the $\text{Mn}_2(\text{OH})_6$ and soon fails to give any yellow tint whatever; further addition of permanganate produces a decided green tint to the liquid part of the mixture. If after a minute or two this remains permanent it may be known that all the copper has been oxidized.

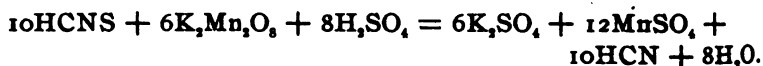
Dilute sulphuric acid (1 : 5) is now slowly added with constant stirring to prevent heating. When the solution becomes clear a decided excess of the dilute acid is added, the whole warmed to 60° or 70° , and the titration continued to the usual pink end reaction. If in this part of the reaction the brown manganic hydroxide does not quickly disappear by solvent action of the acid, it is evidence that the acid is not present in sufficient excess or that the amount started with has been largely exhausted and more acid should be added. Concentrated acid may not, at any time, be added to the solution because of the tendency to form the carbon oxysulphide.

Notwithstanding the above somewhat roundabout reactions,

the whole process proceeds uniformly as if the reaction were simply thus: $10\text{CuCNS} + 7\text{K}_2\text{Mn}_2\text{O}_8 + 21\text{H}_2\text{SO}_4 = 7\text{K}_2\text{SO}_4 + 14\text{MnSO}_4 + 10\text{HCN} + 10\text{CuSO}_4 + 16\text{H}_2\text{O}$. This reaction serves to emphasize two things: first, that much sulphuric acid is needed in the reaction, and second, that the amount of permanganate used is high in proportion to the copper present.

This is further evident when it comes to the matter of calculation. In determining the permanganate factor for copper from its iron standardization it is noted that by the above equation the molecular ratios are: $10\text{Cu} : 7\text{K}_2\text{Mn}_2\text{O}_8$. Comparing with the usual iron ratio 1 : 10, we find the ratio between copper and iron to be $10\text{Cu} : 70\text{Fe}$ or $63.6 : 392$ or 0.1602 . Hence the iron value per cubic centimeter of the permanganate multiplied by the factor 0.1602 will give the copper value per cubic centimeter. While this feature is an advantage where the copper content is low, it also calls for the use of small quantities where the copper content is high, otherwise the consumption of permanganate will be excessive. It is therefore best to weigh out 1 gram of the substance and make up to 250 or 500 cc., and take an aliquot part as seems to be indicated by the depth of color due to the copper present. A decinormal solution of permanganate having an iron factor of 0.0056 would have a copper factor of 0.000897 ; hence, an amount of copper in excess of 40 milligrams would use more than 50 cc. of permanganate.

It may be well to note further that the amount of permanganate used in oxidizing the copper is only about one-sixth of the amount used in subsequent titration; hence, there is little danger of overrunning the total amount in the alkaline part of the process where the end reaction is indefinite. This point is further illustrated by the equation for thiocyanic acid alone, thus:



The process evidently demands that the thiocyanate precipitate be very complete, exact and free from sulphur. That these conditions are easily attainable seems to be indicated by the results. Removal of other metals is not necessary, even silver does not interfere because unaffected by the treatment with caustic alkali, and the insoluble silver thiocyanate acts so very

slowly on permanganate solution as not to vary the end-reaction appreciably. Results have been obtained as follows:

A solution of copper sulphate was made and acidified with nitric acid. Careful electrolytic determination of the copper gave a factor for each cubic centimeter of 0.00661 gram.

Solution taken. cc.	Titration. cc.	Indicated copper in mg. per cc.	Error as referred to electrolytic result in mg. per cc.
(a) 5.....	32.8	6.63	+0.02
(b) 5.....	32.6	6.59	-0.02
(c) 5.....	32.8	6.63	+0.02
(d) 5.....	32.5	6.57	-0.04
(e) 5.....	32.7	6.60	+0.01
(f) 10.....	65.6	6.63	+0.02
(g) 20.....	130.6	6.59	-0.02
(h) 40.....	372.0	6.60	-0.01

The reaction between a thiocyanate and permanganate seems to be very constant. One exception only has been found and that not necessarily of such a nature as to interfere with the accuracy of the above process.

A solution of 1.5 grams of ammonium thiocyanate to a liter of water has a strength very nearly corresponding to N/10 permanganate solution. Now up to this point of dilution the thiocyanate seems to react regularly and in accordance with the above reactions. If, however, the thiocyanate be largely diluted beyond this point, the amount of permanganate used up in the reaction is appreciably less than the same quantity of thiocyanate would use, if undiluted. For example, a measured quantity, say 10 cc., of thiocyanate, if diluted 200 times, will titrate approximately 0.1 cc. of N/10 permanganate less than the same solution would use if undiluted.

This tendency to a lower titration seems to be corrected by acidifying more strongly with acid to correspond with the dilution; also in a less degree by somewhat higher heat.

Such possibility of error, however, is easily guarded against by keeping the solution of copper and thiocyanate in a concentrated form, or rather refrain from diluting the mixture, the necessary reagents alone furnishing all needed dilution from the time of treating the asbestos pulp and precipitate with alkali to the final titration with the permanganate. I desire to acknowledge my obligation to Mr. A. R. Johnston for the analytical data connected with this work.

FREE ARSENIOS OXIDE IN PARIS GREEN.

BY E. W. HILGARD.

Received July 6, 1900.

IN view of the many reclamations and conflicting results as to the content of free arsenious oxide in commercial Paris green that have reached this station since the publication of Bulletin No. 126, in which the unsatisfactory quality of the average material now on the market was discussed, it seems desirable to review briefly some of the causes of the discrepant results of different analysts.

The serious injury to foliage frequently resulting from the use of the commercial article led this Station to investigate specially the subject of the presence and correct determination of free As_2O_3 . It should be understood that in the arid climates, where practically no rain falls during the summer, the absence of the periodic washing-off of the leaves, such as frequently recurs in the region of summer rains, permits of injury from a much smaller percentage of the free arsenical compound. The limit above which such injury occurs was found by our experience to be 4 per cent. of free arsenious oxide; and whenever that amount is exceeded we recommend the addition of a certain proportion of slaked lime to counteract its effects.

The New York law requiring the total percentage of arsenious oxide in Paris green to be "not below 50 per cent.," wholly omits any reference to the free or combined state of the compound. Hence some manufacturers have discarded all care in this respect, and greens containing as much as 20 per cent. and more, of the free oxide, are of frequent occurrence. Such articles are extremely objectionable in this climate at least, and probably elsewhere. This law certainly needs amendment, as it puts a premium on careless manufacture, or fraud. In some samples submitted to us it was evident that the "white arsenic" had been added in bulk to the green, as in the case of other adulterants, among which gypsum, Glauber's salt, chalk, and pipe-clay were easily identified by the microscope as well as by chemical tests. Microscopic examination proved, in fact, to be such a convenient and decisive test in most cases, that it is

always the first thing we do, as it frequently renders any further chemical work wholly unnecessary. The cogency of the microscopic examination is not so generally appreciated by chemists as it is by mineralogists; but there is no excuse for any mistakes in such work, as the crystalline forms of adulterants are perfectly conclusive, either directly, or after solution and evaporation. Especially can there be no mistake about the lustrous, sharp octahedrons of arsenious oxide, whether they be scattered about among the globules of Paris green, or, as is most commonly the case, adherent to the surface of the latter; so that in case of large proportions of the free arsenic, the globules are set with sharp octahedrons like a circular stone-saw or "diamond-drill." In most of such samples we have found the bulk of the free arsenic to be in this condition.

Such crystals dissolve very slowly in cold water, and even when 40° or 50° C. is used; and as a high temperature disintegrates the green globules, it does not seem admissible to employ it. After twenty-four hours' treatment with indefinite quantities of cold water, the arsenical crystals were sometimes still discernible as transparent, obtuse ridges around the outside of the globules, still constituting quite one-half of the total free arsenious oxide.

It is thus obvious that by treatment of Paris green for a few hours, with such small amounts of water as we find are in use at some of the Eastern stations (100 to 300 cc. per gram of green), too low results must be obtained. As in orchard practice the proportion of water used is from 500 to 1000 times the weight of the green employed, it seems proper to conform the analytical practice to this practice, in order to obtain results that shall represent the actual facts of the case. This is what we have adopted as a rule, together with the prolonged agitation of the green with the water, which is likewise practiced in the orchard. It is from this cause, doubtless, that our results are almost uniformly above those of our Eastern colleagues; but I think we are justified in adhering to what is manifestly in accordance with the practical outcome. It has been repeatedly said to us, in reply to our insistence on the microscopic examination, that "no Eastern chemist practices it." To this I have only to say, that in this as in numerous other cases, the microscopic examination usually affords so much more prompt and decisive informa-

tion regarding purity or adulteration than mere analysis, that I cannot but regard its omission as a serious mistake, in neglecting important evidence so readily obtainable.

It has been suggested that we do not take into account the "solubility of Paris green in water," as estimated from the amount of copper going into solution. But as in several cases we have found verdigris to pass into the first filtrates, the dissolution of copper being reduced to a mere trace when the washing was continued beyond 1000 cc. per gram, it is manifest that this correction cannot be applied safely without special precautions, even if it were certain that Paris green is soluble; in any case, the arsenic that passes into solution in this form cannot exceed a fraction of 1 per cent. In the case of a sample containing somewhat less than 4 per cent. of free arsenious oxide, for which an Eastern chemist has reported only 0.9 per cent., we found in the first 1200 cc. applied to 1 gram of substance, 0.26 per cent. of copper, for which, supposing it to represent Paris green, a similar weight of arsenious oxide would have to be deducted. But an additional 600 cc. failed to give *any* reaction for copper, even when concentrated to 25 cc., although a small amount of arsenic still continued to come. The microscope showed the cause of this continued slight contamination to be a few readily recognizable octahedrons of arsenious oxide adherent to the surface of the globules, here and there. Practically the same results were obtained by a slow percolation of cold water, when after the passage of 2000 cc. no copper reaction could be found; but a trace of arsenic continued to come through at the end of the fifth liter of water. In the sample thus washed, however, no arsenical crystals could be detected by the microscope, but only fragments of crushed globules of Paris green, whose form and aspect cannot be mistaken for arsenious oxide by any practiced eye.

It is thus obvious that extraction with a few hundred cc. of water for a few hours cannot yield a proper measure of the free arsenic present in Paris green. Not less than 600 cc., and preferably not less than 1000 cc., or 1 liter per gram, should be employed, and the extraction continued for twenty-four hours.

As to the test prescribed by at least one Eastern station, *viz.*, the solubility of the pure green in ammonia, it is utterly illusory

so far as "white arsenic" is concerned. Even if the latter were not itself rather readily soluble in ammonia, the fact stated in all books of reference that it is easily soluble in ammonium arsenite (which is of course formed when Paris green is dissolved in ammonia) fully disposes of any claim of this test to acceptance.

UNIVERSITY OF CALIFORNIA, June 30, 1900

A METHOD OF DETERMINING FREE ALKALI IN SOAPS.

BY R. E. DIVINE.

Received July 26, 1900.

THE usual method of making this determination prescribes a separation of caustic from carbonated alkali by drying the soap, dissolving in absolute alcohol, and after filtering and washing the undissolved carbonate with alcohol and dissolving in water to titrate the solutions containing caustic and carbonate, respectively, with standard acid. This method is open to several objections, aside from the amount of time consumed. If it is desired to obtain accurate results on the caustic and carbonate separately, the preliminary drying of the soap introduces an error since the caustic alkali will take up carbon dioxide from the air unless the drying is done out of contact with air. It is quite a troublesome process to filter an alcoholic soap solution if one is not provided with appliances to keep the funnel hot during filtration. Dudley and Pease¹ use an alcoholic solution of stearic acid for titrating the caustic, but still filter from undissolved carbonate, and determine the latter in the usual manner. In the following process the writer has succeeded in eliminating filtration. For this method it is necessary to provide three standard solutions:

1. Hydrochloric acid, $N/10$ (for standardizing 2).
2. Caustic soda, $N/10$, in alcohol.
3. Stearic acid, $N/10$, in alcohol.

2 and 3 should be exactly equivalent one to the other, titrated warm with phenolphthalein indicator.

Two grams soap (which needs no drying) is weighed into a round-bottomed flask, of about 300 cc. capacity, and 50 cc. alcohol poured upon it. $N/10$ stearic acid is now run in from a

¹ *Engineering and Railroad Journal*, (1891), 551.

burette in amount judged to be sufficient to neutralize the free alkali in 2 grams of the soap, some phenolphthalein added, and the flask then stoppered with a cork stopper, through which passes a glass tube about 30 inches long and of about $\frac{1}{4}$ inch internal diameter, the lower end ground to a point on a grindstone, and the purpose of which is to serve as a reflux condenser. The flask and contents are placed on a steam-bath and heated thirty minutes, at the expiration of which time the solution should be quite clear and show no alkali with the phenolphthalein. If the solution turns red during the boiling, showing that an insufficient quantity of stearic acid has been added at first, add more of that solution until the color disappears, then several cubic centimeters in excess, and heat twenty minutes further. The flask is now removed from the bath and, after a few minutes' cooling, titrated with N/10 caustic soda. The difference between the number of cubic centimeters stearic acid solution added and the number of cubic centimeters caustic soda used to back titrate is equivalent to the total free alkali present.

While the first flask is heating, weigh out in a similar flask 2 grams of soap and add 50 cc. alcohol and place on the steam-bath. When the first test is finished, calculate roughly the total alkali, assuming the total quantity to be carbonate. Now add to the second flask an amount of 10 per cent. barium chloride solution sufficient to precipitate alkali found,¹ heat a few minutes, add phenolphthalein, and titrate with N/10 stearic acid. The titration must take place slowly and with thorough agitation of the liquid for the reason that the sodium or potassium hydroxide reacts with the barium chloride added and forms sodium chloride and barium hydroxide. The latter is not very soluble in the alcoholic liquid and sufficient time and pains must be taken to ensure its complete neutralization by the stearic acid. A blank test should be made on 50 cc. of the alcohol, since this frequently contains carbon dioxide, and the number of tenths cc. N/10 caustic soda necessary to neutralize the free acid in this quantity of alcohol added to the reading of the stearic acid burette in the second test. This corrected reading gives the number of cubic centimeters N/10 stearic acid used to neutralize the caustic alkali in 2 grams of soap. The difference between the total

¹ 1 cc. N/10 stearic acid = 0.0125 gram $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ or 0.125 cc. 10 per cent. barium chloride solution.

alkali found and the caustic will, of course, give the carbonate. For example : 2 grams of soap and 15 cc. N/10 stearic acid ; run in 3.2 cc. N/10 caustic soda to back titrate. Consequently, $15 - 3.2 = 11.8$ cc. N/10 stearic acid equivalent to total free alkali.

To neutralize the caustic in the sample treated with barium chloride was required 4.1 cc. N/10 stearic acid. Fifty cc. of the alcohol used required 0.2 cc. N/10 caustic soda, then $4.1 + 0.2$.

4.3 cc. N/10 stearic acid to neutralize free caustic alkali.
 $11.8 - 4.3 = 7.5$ cc N/10 stearic acid to neutralize carbonated alkali.

1 cc. N/10 stearic acid = 0.004 gram caustic soda or 0.0053 gram sodium carbonate.

The above figures calculated to percentage would be :
0.86 per cent. caustic soda and 1.99 per cent. sodium carbonate.

It is to be noted that a rubber stopper cannot be used in the flasks for dissolving the soap on account of the sulphur in the rubber, which decolorizes an alcoholic solution of phenolphthalein. The method is applicable to all soaps which do not contain fillers which react with the standard solutions employed.

BUFFALO, July 24, 1900.

INVESTIGATIONS ON THE DETERMINATION AND COMPOSITION OF HUMUS AND ITS NITRIFICATION.

BY CHARLES RIMBACH.

Received July 30, 1900.

THE investigation on the nitrification of the *matière noire* of Grandeau, here discussed, was undertaken on the suggestion of Prof. Hilgard, to test the question whether or not that substance is to be regarded as a source of nitrates under the influence of nitrifying bacteria as has been assumed, but never definitely proved. The method of preparation consists in treating the soil with dilute hydrochloric acid to remove the lime and magnesia with which the humus substance forms insoluble compounds ; and after washing with distilled water, until the filtrate is neutral, extracting it with 6 per cent. ammonia. On evaporation the solution leaves the *matière noire* behind.

As a medium containing the carbonates of lime and magnesia is most favorable to nitrifying bacteria, the compound of the

humus with these metals was employed for the experiment in order to simplify conditions. For this purpose the ammonia extract from a soil was precipitated with hot solutions of gypsum and magnesium sulphate; the compound, which settles very slowly, was washed and decanted several times with gypsum solution to keep it flocculated, and then put on a linen filter. After the liquid had passed, the mass was further washed by shaking up in a bottle with gypsum solution, this operation being repeated until the filtrate was nearly colorless. The precipitate was dried at 100° , whereby it lost considerably in volume, forming a hard, brilliant, brittle mass with conchoidal fracture. It was free from ready-formed ammonia expellable by magnesia. The lime-magnesia compound thus prepared naturally contained gypsum. In the air-dried condition the precipitates prepared from two different soils had the following composition:

West Berkeley Soil.—An excessively stiff clay or "black adobe" soil, rich in lime, containing over 2 per cent. of *matière noire*.

CALCIUM-MAGNESIUM HUMATE.

	Per cent.
Water	17.95
Ash	14.34
Organic matter.....	67.71
Nitrogen	3.06 of the organic matter.

Redwood Soil.—From Marin County (sandy humus soil).

CALCIUM-MAGNESIUM HUMATE.

	Per cent.
Water	17.80
Ash	15.37
Organic matter.....	68.57
Nitrogen	4.01 of the organic matter.

The ash of the latter was soluble in dilute hydrochloric acid, leaving an insignificant white residue. It contained:

	Per cent.
Lime.....	47.07
Magnesia.....	13.65
Phosphoric acid	6.15
Potash in noticeable quantity.	

The humate from the Redwood soil, being the richer in nitrogen, was used for the nitrification experiment. Twenty-eight grams humate = 22.8816 grams dry matter with 0.767 gram nitrogen, were mixed in a beaker with 2 kilos of sand taken from drifting sand dunes, a short distance from the ocean near San Francisco; it had been previously ignited, and freed from nitrates by leaching with hydrochloric acid and distilled water.

The material for infection was prepared from soil of the ten-acre tract, Southern California Experiment Station. This soil contains from 1,560 to 12,280 pounds of alkali salts per acre to the depth of 1 foot; up to 23 per cent. of these are nitrates = 0.062 per cent. of the soil. After having been freed from nitrates by washing with distilled water, it was shaken with water, and the turbid liquid filtered through linen; the above mixture was moistened with the filtrate.

The material was kept for two months at a temperature of about 25°. Every other day, with some interruptions, the sand was moistened so that the content of free water amounted to about 2 per cent., stirred up with a glass rod, and thus kept in a mellow, flocculated condition, to facilitate the access of the air. After that lapse of time the moistened sand was mixed thoroughly, and a part of it was dried, weighed, and leached with water. The extract, subjected to the colorimetric determination of nitric acid, showed that 5.94 per cent. of the nitrogen of the humus substance had been nitrified.

Further experiments are in progress for comparing the nitrification in a natural soil, and in the same freed from *matière noire*, in which the microscope showed only slightly browned vegetable débris.

Conclusions.—The assumption made heretofore by Prof. Hilgard and others that Grandeau's *matière noire* is a direct source of nitrogen through nitrification, is definitely verified by the above experiment, in which all other possible sources were eliminated. It also justifies, presumptively, Prof. Hilgard's thesis that humus containing a high percentage of nitrogen, such as is found in the soils of the arid regions, will yield larger amounts of nitrates in the same time than will that of lower nitrogen percentages; and that conversely, low nitrogen percentages may fail to supply a sufficiency for plant growth.

*Determination of Humus.*¹—An investigation was also made to test the Grandeau method for the determination of humus, and particularly that of nitrogen in humus, as hitherto used. The method is the following :

Two portions of 5 or 10 grams of air-dried soil are weighed off into prepared filters. They are treated with 1 per cent. hydrochloric acid to dissolve out the lime and magnesia, as already explained. The treatment with acid is continued until there is no reaction for lime ; the acid is then washed out with water to neutral reaction. The funnels containing the washed soils are now stoppered and one of them is treated with ammonia water (6 per cent.) for the determination of humus by evaporation, and the other with sodium hydroxide (4 per cent.) for the estimation of nitrogen. The lye, whether ammonia or soda, remains in the respective funnels a few hours ; the solution is then allowed to pass through and the filter washed once with the lye ; the funnel is then restoppered and a fresh quantity of the solvent put on the filter. The treatment is repeated until the filtrate remains colorless. The solutions are then made up to 1 liter, and aliquot parts are taken for the determination.

The ammonia solution is evaporated in a weighed platinum dish, the residue dried at 100°, weighed, ignited, and reweighed, the loss in weight showing the amount of humus.

The soda solution is treated with sulphuric acid and mercuric oxide to determine the nitrogen in the usual way.

The percentage of nitrogen in the sodium extract is referred to the percentage of humus in the soil as determined by ammonia extraction, for obtaining the percentage of nitrogen in the humus.

It was to be decided whether, as assumed in this method, ammonia and soda extract the same quantities of humus and nitrogen ; *i. e.*, the same substances. For this purpose two soils, peaty soil from Westminster, Orange Co., Cal., with 19.12 per cent. humus, and heavy black adobe soil from the University grounds with 1.20 per cent. humus, were treated as above described. A duplicate of the Westminster soil served for determining the quantity of humus lost for the analysis by the extrac-

¹ The word "humus," as used in this paper, is intended to designate Grandeau's *matière noire*.

tion with hydrochloric acid and water, which was prolonged until 1 liter of filtrate was obtained. Three hundred cc. of this filtrate on evaporation gave 0.0375 gram residue, containing 0.0367 gram organic matter with 7.45 per cent. nitrogen. This quantity of organic matter is 4.53 per cent. of that contained in the ammonia extract.

For determining the organic matter of the ammonia solution, aliquot parts of it were evaporated. The residue always contains combined ammonia, which was determined in another aliquot part (previously boiled to expel free ammonia) by distillation with magnesia. The quantity found, subtracted from the loss of weight by ignition, gives the organic matter. In the residue from the distillation the organic nitrogen was determined by the Kjeldahl method.

	Gram.
Residue of 200 cc. ammonia solution.....	0.1795
Ash	0.0108
Ash-free ammonia humate.....	0.1687
Less combined ammonia.. ..	0.00834
Organic matter.....	0.16036

The combined ammonia taken up from the ammonia solution amounts to 4.93 per cent. of the ash-free ammonia humate; the organic nitrogen, to 6.98 per cent. of the organic matter.

The determination of the organic nitrogen in the ammonia and soda solutions respectively, when applying the above correction, gave the following results:

	Mg.
Organic nitrogen in 100 cc. ammonia solution.....	5.33
Organic nitrogen in 100 cc. soda solution.....	8.23

These results are important in that they prove that soda solution extracts more nitrogen than does ammonia.

On account of the impossibility of determining the organic matter in the neutralized soda solution by evaporation and calcination, because of the large quantity of sodium salt, which hinders the combustion, it was decided to determine by the precipitation of the humus, the quantity and quality of humus-substances in both extracts. In order to determine which reagent precipitates the humus most completely, ammonia-humate extract from University adobe soil was treated with solutions of copper and magnesium sulphates, and with hydrochloric acid. Before adding the salt solutions, the humus

extract was freed from uncombined ammonia by boiling; the precipitates were washed with boiling water, in which the magnesium humate was rather soluble, while the filtrate from the copper humate was perfectly clear and nearly colorless. The hydrochloric precipitates were washed with 2 per cent. hydrochloric acid until 500 cc. had passed. All precipitates were free from ammonia. The nitrogen content of the filter was considered. For all precipitations the same quantity of ammonia extract was used.

	Precipitants used.		
	Copper sulphate.	Magnesium sulphate.	Hydrochloric acid.
Organic matter of the precipitates in per cent. of the total organic matter of the extracts	89.16	65.16	85.21
Nitrogen of the precipitates in per cent. of the organic matter of the precipitates.....	4.48	4.93
Nitrogen of the precipitates in per cent. of the total organic nitrogen of the extract..	88.24
Ash in per cent. of the precipitates.....	23.40	14.60	5.21

These results show that magnesium sulphate (because of the solubility of humates in water) is not suitable as a precipitant, while copper sulphate precipitates the humus-substances most completely. Hydrochloric acid has nearly the same complete effect as copper sulphate, and as it can be added to the extract without previous elimination of ready-formed ammonia, it was used for the determinations described above.

The precipitation of the humus with hydrochloric acid in the ammonia and soda extracts from the Westminster and University soils, gave the following results :

		Nitrogen of the precipitates in per cents of			
		Precipitate of the humus acids by hydrochloric acid.	Organic matter of the same.	the organic matter of the precipitates.	the total organic nitrogen of the extract.
<i>Westminster Soil—</i>		Gram.	Gram.		
Ammonia solution..	200	0.1127	0.2110	5.84	54.78
Soda solution	200	0.1495	0.1490	3.75	22.78
<i>University Soil—</i>					
Ammonia solution..	300	0.0299	0.0233
Soda solution.....	300	0.0103	0.0077

It is thus seen that the humus-substances of these two soils behave altogether differently toward ammonium and sodium hydroxides as solvents.

The nitrogen of these precipitates was not determined on account of the small amounts obtained. The organic matter of the hydrochloric acid precipitate from the Westminster ammonia solution is 70.24 per cent. of the total quantity of organic matter contained in the same.

Even if the chlorides of ammonium and sodium should influence differently the solubility of the precipitates, the ratio of the latter, which is 3 : 4 in the first, and 3 : 1 in the second case, shows that substances of different nature are thus obtained.

Organic Matter in the Soda Extract.—For determining approximately the ratio of nitrogen and organic matter in the soda extract, a weaker solution, which, of course, may have a different solvent power, was used in the extraction. 140 grams of University adobe soil, after being extracted with hydrochloric acid and water (250 cc. of the latter contained 0.0133 gram organic matter) was treated during twelve hours with 1 per cent. soda solution, then washed with 0.25 per cent. soda-lye, this operation being repeated until 1 liter filtrate was reached. 50 cc. of this were evaporated, the residue ignited, a solution of ammonium carbonate added in order to convert lime and magnesia into insoluble carbonates, evaporated again, and the residue gently heated. Then the ash was extracted with water and the quantity of sulphuric acid necessary for neutralizing the soda determined by titration. With the same quantity of acid 50 cc. of the soda solution was evaporated. The residue dried, weighed, ignited, and reweighed showed the organic matter. The determination of nitrogen was made with an aliquot part.

For comparison, 140 grams of the same soil were treated with the same quantities of acid, water, and 6 per cent. ammonia, and the extract was analyzed in the usual way. The ash-free residue contained 5.88 per cent. of ready-formed ammonia.

	cc.	Organic matter. Gram.	Organic nitrogen in per cents. of the organic matter.
Ammonia solution.....	50	0.0589	4.73
Soda solution.....	50	0.0543	5.37

These figures, however, do not allow a definite conclusion as to the total amount of soluble humic matter in the soil : for it was found that in the ammonia filtrates obtained at different times during the extraction (which lasted six days), the nitrogen percentages of the organic matter vary considerably. The differences in the percentages of combined, ready-formed ammonia are small.

AMMONIA SOLUTION FROM SOIL FROM THE TEN-ACRE TRACT.

	Organic nitrogen. ¹	Combined ammonia. ²
Filtrate from the first four hours....	4.90	6.75
Filtrate from the seventh and eighth day	9.35	7.26

Apparently the humus-substances that are poor in nitrogen are readily soluble in ammonia and consequently form the main part of the first extract, while the substance with higher nitrogen percentages are less soluble and need a longer time for entire extraction by ammonia, but are more quickly dissolved by soda.

CONCLUSIONS.

1. By leaching with hydrochloric acid and water a certain quantity of humus, varying in the different soils, is lost to the subsequent extraction with ammonia.

2. The content of nitrogen of the soda extract, being different from that of the ammonia extract, cannot be directly referred to the content of organic matter of the latter.

3. In the determination of organic matter and nitrogen in the ammonia extract, the quantity of combined ammonia must be considered, as has been described in the analysis of Westminster humus.

It is thus evident that the percentages of humus heretofore determined are too high, inasmuch as the combined ammonia, which is about 5 per cent. of the ash-free ammonium humate, has been erroneously calculated as organic matter. Furthermore, if all soils behave like Westminster soil, from which soda extracts about one and a half times as much nitrogen as does ammonia, the nitrogen percentages in humus as heretofore determined, even though they are referred to organic matter and combined ammonia, would be too high.

¹ In per cents. of the organic matter contained in the solution.

² In per cents. of the ash-free ammonia humates.

4. The question still remains whether soda or ammonia solution, and in what strength, satisfy best the requirements of a solvent for humus substance, regarded as the sum of organic substances; decomposed or not, that are immediately available for the plants.

After concluding this investigation, we received a publication of A. L. Emery entitled "Soil Humus: Some Sources of Error in Analytical Methods." As to the absorption of ammonia by the humus solution, there mentioned, it is, as we have explained, at least partially a simple process of combination of the humus acids (liberated by hydrochloric acid from earth bases) with the ammonia; the quantity of the latter has been regularly determined by Prof. Hilgard for some time past, by distillation with magnesia (not lime, which decomposes organic nitrogen compounds). A question, however, still to be decided is whether the ammonia used forms amido-compounds with the humus substances during the digestion or evaporation.

NOTES.

The Brown-Taylor-Richards Method for the Microscopical Identification of Butter.—In the June number of the Journal appears an article by John A. Hummel on "Brown and Taylor's Official" method of identifying butter, with plates showing the appearance of butter, oleomargarine, and renovated butter, when viewed by polarized light. This is the first time the method used by the Bureau of Internal Revenue for identifying oleomargarine has been formally christened, and I would suggest, if the designation is to stand in chemical literature, the addition of the name of Mr. Richards, formerly microscopist of this office, to whom is due the credit for its adoption and successful employment as a field test for the past twelve years. His report on this subject will be found on page CLXII of the Annual Report of the Commissioner of Internal Revenue for the fiscal year ended June 30, 1888. Directions for the use of the form of (unmounted) microscope officially adopted and its polarizing attachments are given in Series 7, No. 9, revised, of the Regulations of the Internal Revenue Office, everything being simplified as much as possible, so that the test can be performed by

* ¹ This Journal, 22, 285 (1900).

persons not specially skilled in microscopical manipulation. These regulations, which are in the hands of all internal revenue officers, contain plates prepared by Richards showing the appearance of oleomargarine when viewed by polarized light, presenting the same characteristics as are given by the plates in Hummel's article, except that no reproduction is made of the appearance of butter, since this is, practically, a blank field.

In regard to the use of this test to distinguish between fresh and renovated butter, the experience of this office would tend to substantiate strongly the claims for its value put forth by Hummel. The regulations above referred to recognize the fact that it is really a test for the presence of melted fat, and prescribe that all samples giving a doubtful appearance in the microscope shall be sent in to Washington for a chemical examination. Of those which proved to be butter when thus examined, about nine-tenths are renovated butter, showing a field more or less mottled when examined with crossed nicols. In fact the value of the method as a sorting test to discriminate between butter and oleomargarine has been seriously impaired of late years by reason of the large quantity of renovated butter which has found its way into the markets. This is mainly due, however, to the lack of skill on the part of revenue officers, few of whom have occasion to make frequent use of the instrument. To a person skilled in the use of the polarizing microscope, it is not difficult to distinguish between oleomargarine and melted butter, for it is seldom a sample of the latter is met with which gives the sharply defined, crystalline appearance of the field typical of most oleomargarine. In applying the method to the identification of renovated butter much care should be exercised, for, in my experience, most butters will show *some* variation in the field, due probably to a slight crystallization at some period in their production, and it is rare indeed to find a sample giving the uniformly blank field implied by Hummel's plate of "normal butter."

The method certainly deserves mention along with the tests given by Hess and Doolittle,¹ the best of which is the "spoon test" (the absence of froth in oleomargarine or renovated

¹ This Journal, 22, 150.

butter when heated in an open receptable) which has been in use for the detection of oleomargarine for many years, and which is preferred by some revenue officers to the microscope test.

C. A. CRAMPTON.

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DEPARTMENT, WASHINGTON, D. C.

The Analysis of Arsenical Insecticides.—Since sending my article¹ on "The Adulteration and Analysis of the Arsenical Insecticides" to press I have done still further work on the soluble arsenious oxide in Paris green, and find that although an extraction of 1 gram of Paris green with 500 cc. of water finally gives practically constant results, still a small amount of cupric oxide goes into solution at the same time, thus indicating that either the Paris green itself is soluble in cold water or breaks up slightly on treatment with this medium. I am inclined to think that this last assumption is the more likely, since the amount of copper oxide going into solution in the 500 cc. of water is not constant.

If we assume then that the Paris green breaks up, and that for a certain amount of copper oxide a corresponding amount of arsenious oxide goes into solution, the figure obtained for soluble arsenious oxide (without taking into consideration the breaking up of the Paris green itself) which we will call the *apparent* per cent. of arsenious oxide, will not represent the *actual* per cent. of arsenious oxide, but a determination of the copper oxide dissolved in the water will have to be made, and after calculating how much arsenious oxide this corresponds to, the resulting figure will be subtracted from the *apparent* per cent. of arsenious oxide, thus leaving the *actual* per cent. of free arsenious oxide in the green.

It is of course possible, even probable, that the arsenious and copper oxides of Paris green do not go into solution in water in the same proportion that they are present in the original compound, but in the present state of our knowledge it seems to be the most plausible assumption that they do.

The determination of copper oxide is made by precipitating an aliquot portion of the 500 cc. of cold water extract with hydrogen sulphide, filtering, washing and drying the combined sul-

¹ This Journal, 22, 568.

phides of arsenic and copper, burning the precipitate and filter with powdered sulphur, and finally weighing as the mixed oxide and subsulphide of copper. On ten samples of Paris green the following results were obtained:

No.	Apparent per cent. of arsenious oxide extracted.	Per cent. of copper oxide extracted.	Arsenious oxide corresponding to copper oxide extracted.	Actual per cent. of arsenious oxide in Paris Green
1.....	5.81	0.80	1.50	4.31
2.....	9.69	0.55	1.03	8.66
3.....	4.60	0.70	1.31	3.29
4.....	4.60	0.60	1.12	3.48
5.....	4.11	0.65	1.21	2.90
6.....	3.63	0.50	0.94	2.69
7.....	7.75	1.35	2.53	5.22
8.....	6.54	0.70	1.31	5.23
9.....	10.65	0.45	0.84	9.81
10.....	5.57	0.90	1.69	4.88

J. K. HAYWOOD.

On Carborundum.—In a paper on carborundum (carbide of silicon), read at the World's Congress at Chicago in 1893, and published later in this Journal,¹ there appeared in the second paragraph the following statement :

"It is an American invention, having been discovered by Edward H. Acheson, of Monongahela City, Pa., who carried the invention to commercial success with extraordinary energy in the face of many obstacles."

As a part of the discussion at the close of the paper, I asked the author if he was aware that an electric furnace precisely similar to the one he had described was fully protected by letters patent issued to Messrs. Eugene H. and Alfred H. Cowles, in 1884. I further asked him whether the author was aware that in 1885, the substance to which had recently been assigned the name carborundum, was made in the Cowles furnace, and that specimens of this material could be found in several museums throughout the country. The author disclaimed any knowledge of such a furnace, or that any such material had been produced prior to that produced by Mr. Acheson.

In the United States Circuit Court of Appeals for the Third Circuit (Judges Dallas, Gray, and Bradford), a decision has

¹ This Journal, 15, 411.

just been rendered (May 28, 1900) in a case of infringement, in favor of the patent granted to A. H. and E. H. Cowles, Dec. 24, 1884, and against the patent of E. H. Acheson, alluded to above.

In stating the ground of their decision, the judges make the following statement: "There can be no doubt on the evidence that prior to the process patent in suit metallurgical operations had been performed through the instrumentality of the electric arc, electrical conductors consisting of wires or rods of metals, or of other solid or concrete bodies, or by electrolysis. But on careful examination we have failed to find any patent, publication, or other matter alleged as an anticipation, or as showing the prior art, a practical process for metallurgical or analogous operations involving the use of a discrete body of conductive, but resistant material rendered incandescent by the passage of an electric current, and mixed or otherwise in contact with the material to be treated. This is the broad, underlying idea of the process patent in suit, and is covered by its claims. The Messrs. Cowles were the first to invent and use this process, and the patent must be sustained. It is a meritorious one, and its claims are entitled to considerable liberality of construction." This decision gives priority broadly to the Messrs. Cowles for reducing ores and other substances by the incandescent method.

CHARLES F. MABERY.

CLEVELAND, June 5, 1900.

NEW BOOKS.

THE CHEMISTRY OF THE METALS. BY J. H. KASTLE. Lexington, 1900. vi + 198 pp. 8vo.

The author of this book admits in his preface that the number of text-books on general chemistry is so great that "the burden of proof certainly rests upon any new writer who ventures into this field to show that anything new in this line is deserving of publication," and makes a plea for the fuller study of the metals, bodies that constitute two-thirds of the elements. The author says: "An attempt has been made to supplement the laboratory work on each family of metals with a general presentation of the subject according to the Periodic Law."

Chapter I opens with general elementary statements as to the

differences between mixtures and compounds, analysis, synthesis, and chemical study of a substance; in successive chapters are given descriptions of the metals taken by families and by groups so as to avoid unnecessary duplication, extending from the alkalis to iron, nickel, and cobalt. Following the descriptive portion of each chapter are sections prescribing "Laboratory Work;" these sections consist chiefly of series of questions and in them lies the principal claim to originality for the volume. The queries are intended to make students think for themselves, but sometimes are singularly elementary; thus, following several pages describing the character of the metal magnesium, students are asked—"Is magnesium a metal?" "Is it heavy or light?" "What is its color?" (p. 47). After comparing granite and mercuric oxide, students are asked—"How could you make mixtures?" Yet some of the queries are difficult and would require examination of larger treatises.

To use this volume for instruction, the students must have previously become acquainted with the gaseous elements, the principal acids of inorganic chemistry and the rudiments of qualitative analysis, yet the primary principles of chemistry are laid before them with minutiae that would seem unnecessary had they mastered them previously. At the same time students are directed to make certain experiments, and the instructions given are hardly sufficient. On page 5, for example, students are told to heat HgO in a hard glass tube and to collect the gas evolved over water, but how to arrange this is not mentioned, nor is there any wood-cut of apparatus to illustrate the operation; indeed, illustrations are entirely wanting throughout the volume.

A blemish in the manufacture of the book is due to the carelessness of the printer; paper of uniform color and glaze is not used throughout; page 112 is of a bluish tint, and page 113 of a decided yellow hue. There is no index.

H. CARRINGTON BOLTON.

ERRATA.

In Vol. 22, page 573, line 23, for "sodium acetate" read "sodium arsenate;" page 576, line 28, for "really" read "nearly."

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[CONTRIBUTION FROM THE NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION.]

METHODS OF DETERMINING PROTEID NITROGEN IN VEGETABLE MATTER.

BY G. S. FRAPS AND J. A. BIZZELL.

Received August 10, 1900.

THE method usually used for the determination of proteid nitrogen, is that modification of the Ritthausen method proposed by A. Stutzer,¹ which consists in precipitating the proteids with copper hydroxide, and determining the nitrogen in the precipitate. This method has been adopted by the Association of Official Agricultural Chemists, and is in use by chemists generally.

Mallet² has recently proposed that the proteids be precipitated with phosphotungstic acid at 90° C., using in addition tannic acid when peptones are present.

Wiley³ determines the proteids in animal materials by precipitating them with bromine.

The work here to be described is a study of the applicability of phosphotungstic acid and bromine as precipitants for the proteids of vegetable materials.

¹ *Jour. f. Landw.*, 28, 103.

² Bull. 54, Division of Chemistry, U. S. Dept. of Agr.

³ Bulletin 54, Division of Chemistry, U. S. Dept. of Agr.

THE PHOSPHOTUNGSTIC ACID METHOD.

The method as proposed by Mallet is, briefly, as follows: The sample is digested with hot water, filtered on a nitrogen-free filter, and washed with hot water containing a little free acid so long as it gives up soluble matter in sensible amount. It is not advisable to use hot water at first when much starch is present. The filtrate is made slightly acid with acetic acid, heated to about 90° , and filtered. To the second filtrate an acidified solution of phosphotungstic acid is added so long as a precipitate continues to be formed, avoiding any large excess of reagent, the liquid heated to about 90° , filtered, and the precipitate washed with water of about the same temperature. The nitrogen in the precipitates is determined by the Gunning-Kjeldahl method, and calculated to proteids. When peptones are present they are precipitated with tannic acid from the solution which has been acidified with acetic acid. When proteoses are present it may be well to make a check determination of their amount by saturation of the aqueous solution, after acidification with acetic acid, heating and subsequent cooling, with zinc sulphate, and determining nitrogen in the precipitate. It may be well to remove fat when it is present in large quantity.

METHOD MODIFIED.

The method above described involves three, or, if peptones are present, four filtrations, which make it very long and tedious. The object of the precipitation with acetic acid is to reduce the bulk of the subsequent phosphotungstic acid precipitate, out of which the amides are to be dissolved by hot water. Its use is unnecessary. When the above method was followed it was found impossible to get a clear filtrate from most of the vegetable materials tested, although various modifications were tried. At 60° , however, no such difficulty was encountered, although at a slightly higher temperature—depending on the material—turbidity would begin to appear. It was also found that between 60° and 100° , a considerable portion of the nitrogen goes into solution. For this reason the temperatures of 60° and 100° were selected for further tests, 100° giving the maximum turbidity and minimum amount of nitrogen, 60° the minimum of

turbidity, *i. e.*, a clear filtrate. The method after much experimentation was simplified as follows: 1.4 grams of the substance in a beaker were stirred well with 100 cc. water, the phosphotungstic acid reagent added and the liquid heated. The liquid was kept at the desired temperature (60° or 100°) for fifteen minutes, filtered, the precipitate washed with water at the same temperature, and nitrogen determined in it.

The reagent used was a 5 per cent. solution of phosphotungstic acid in 2.5 per cent. hydrochloric acid; 5 cc. were used for 3 per cent. or less of nitrogen, 10 cc. for 6 per cent., and 15 cc. for 9 per cent.

EFFECT OF REAGENT.

In dealing with vegetable materials it was found impossible to tell when a slight excess of the phosphotungstic acid reagent had been added. The following results were obtained by using different quantities of the reagent, and heating to 60°. The figures are means of two closely agreeing determinations.

NO. 1. COTTONSEED MEAL.

	Nitrogen. Per cent.
10 cc. reagent.....	6.61
30 " "	6.64
50 " "	6.27

NO. 2. WHEAT BRAN.

5 cc. reagent.....	2.07
10 " "	2.08
25 " "	2.11
45 " "	2.09

NO. 3. COWPEA MEAL.

5 cc. reagent.....	3.18
10 " "	3.11
25 " "	3.22
45 " "	3.17

A small excess of reagent does not affect the results. A very large excess affects them in the case of cottonseed meal. It seems that 5 cc. of the reagent are sufficient for any vegetable material containing less than 3 per cent. of nitrogen, 10 cc. for 6.5 per cent., and 15 cc. for 9 per cent.

EFFECT OF TEMPERATURE.

As has already been stated, a clear filtrate could not, as a rule,

be obtained at a temperature much over 60°, and nitrogen goes into solution between 60° and 100°. In cottonseed meal and wheat bran, the greatest amount of solution takes place between 75° and 90°; cottonseed meal gave at 60°, 6.61 per cent. nitrogen; at 75°, 6.58 per cent.; at 90°, 4.94 per cent.; at 100°, 4.22 per cent. Wheat bran at 60° gave 2.08 per cent. nitrogen; at 75°, 2.01 per cent.; at 100°, 1.75 per cent. The amount of nitrogen dissolved between 60° and 75° is very small.

In order to show the solvent action between 60° and 100°, the following figures are given. Of the nitrogen precipitated at 60° in cottonseed meal (No. 1.), 36 per cent. goes into solution at 100°; another sample (No. 2.), 24 per cent.; still another (No. 3.), 21 per cent.; cowpea meal, 9 per cent.; green peas, 7 per cent.; soy beans, 18 per cent.; horn meal, 9 per cent.; linseed meal, 12 per cent.; and dried blood, 47 per cent.

Working with blood at 100°, it was found that 5.97 per cent. (37.31 per cent. proteids) goes into solution between 60° and 100°. This sample of blood contained 13.66 per cent. nitrogen, 13.39 per cent. of it being insoluble in water. The filtrate from 100° phosphotungstic acid method was clear, and remained clear although 5.97 per cent. of proteid nitrogen was therein dissolved. This observation threw doubt upon the basis upon which the phosphotungstic acid method is founded; namely, that the phosphotungstic acid precipitate with proteids is not soluble in hot water. This statement is based upon the observation that "the supernatant liquid remained clear on being heated along with the precipitate and subsequently cooled" The following experiments confirmed this suspicion, and proved that phosphotungstic acid does not completely precipitate proteids at 90° or 100°.

0.35 gram of the materials named below were placed in a Kjeldahl flask, 100 cc. of water and 5 cc. of the phosphotungstic acid reagent added, and the solution heated to 60°. The solution was kept at this temperature for fifteen minutes, filtered, washed with water at the same temperature, and nitrogen determined in the precipitate by the Gunning method. Determinations were also conducted at 90° and 100°. Those at 90° were conducted as the others except that the filtration was proceeded with as soon as that temperature was attained.

Name of material.	Total nitrogen. Per cent.	Nitrogen. 60° phosphotungstic acid method. Per cent.	Nitrogen. 90° phosphotungstic acid method. Per cent.	Nitrogen. 100° phosphotungstic acid method. Per cent.
Casein.....	14.12	14.24	13.24	13.34
Blood albumen .	11.82	11.74	11.26	9.92
Egg albumen...	12.42	12.58	12.38	11.90
Haemoglobin ...	13.40	12.82	11.28	9.20
Blood fibrin	13.94	13.62.	12.60
Gelatin.....	14.98	12.90	11.52

It will be noted that in every case the proteid precipitate was partially dissolved when it was heated. The phosphotungstic acid reagent therefore is of no value for precipitating proteids at 90° or 100°. At 60°—excepting gelatin, and perhaps haemoglobin,—the proteids seem to be completely precipitated.

COMPARISON OF THE MODIFIED PHOSPHOTUNGSTIC ACID AND
THE STUTZER METHODS.

The 60° phosphotungstic acid method has already been described. The following table contains some results obtained by this method together with determinations made by the Stutzer method. The figures are means of two determinations:

Name of material.	Total nitrogen. Per cent.	Nitrogen. 60° phosphotungstic acid method. Per cent.	Nitrogen. Stutzer method. Per cent.
Wheat bran	2.20	2.07	1.79
Corn bran.....	1.54	1.48	1.38
Waste rape.....	3.57	2.32	2.62
Green peas.....	1.76	1.57	1.45
Linseed meal	2.86	2.74	2.62
Cottonseed meal No. I ..	6.80	6.61	6.51
" " No. II .	6.18	6.24	6.17
" " No. III.	6.62	6.48	6.42
Dried blood	13.66	12.82	13.00
Soy beans.....	6.15	5.90	5.97
Horn meal	14.70	13.50	13.00
Cowpea meal.....	3.32	3.18	3.19

It will be noted that this method gives results which are, as a rule, almost identical with those by the Stutzer method, although slightly higher. The mean difference is +0.06 per cent., with a maximum of +0.50 per cent., and a minimum of -0.30 per cent. Neither method gives good results with blood; the filtrate from blood by the 60° phosphotungstic acid method

contained 0.57 per cent. water-insoluble nitrogen, and gave a reaction (with copper sulphate and caustic soda) for proteids, and the copper hydroxide dissolved 0.39 per cent. of water-insoluble protein. With regard to the other materials it is impossible to say which method is correct. The 60° method promises, however, to be of value. It is possible that the determination might be carried on at a slightly higher temperature than this, but hardly over 80° in any case.

PRECIPITATION WITH ZINC SULPHATE.

A comparison was made between the nitrogen precipitated by zinc sulphate and that by the other methods on a few materials. The method was as follows: 1.4 grams of the substance were heated with 100 cc. of water to boiling, allowed to cool, 2 cc. of dilute sulphuric acid (1:4) and 140 grams crystallized zinc sulphate added. It was allowed to stand a day or more, with frequent stirring, filtered, and washed with a saturated solution of zinc sulphate containing 1 cc. of the dilute acid in 50 cc.

Name of material.	Nitrogen insoluble in zinc sulphate. Per cent.	Nitrogen. Stutzer method. Per cent.	Nitrogen. 60° phosphotungstic acid method. Per cent.
Cottonseed meal	6.45	6.51	6.61
Soy beans.....	6.07	5.97	5.90
Blood.....	13.48	13.00	12.82
Cowpea meal.....	3.26	3.19	3.18

The results are higher than by the other methods in three of the four cases, and seem to point to the Stutzer method as being more nearly correct.

EXTRACTION OF WATER-SOLUBLE NITROGEN.

Extraction of a vegetable material with hot water sometimes gives discordant results, as was the case with cottonseed meal. The extraction was performed as follows: 1.4 grams were placed in a beaker with 50 cc. water, stirred well, and allowed to stand one hour. The liquid was decanted through a filter, 50 cc. water added to the residue in the beaker, heated to boiling, filtered, and the residue washed with boiling water. The undissolved nitrogen was, in case (a) 4.54 and 4.68 per cent., mean 4.61 per cent.; in case (b) (6 months later) 4.12 and 4.22 per cent., mean 4.17 per cent.; and case (c) (volume of filtrate

less than in case (b)) 5.55 and 5.67 per cent., mean 5.61 per cent. There is thus a variation of 1.44 per cent. of nitrogen, or 9 per cent. of protein. It is quite possible that had the extracting water been slightly acid the results would have been more uniform.

THE BROMINE METHOD.

Rideal and Stewart¹ have proposed to use bromine as a precipitant for gelatin. Allen and Searle² applied the method to the analysis of meat extracts. Wiley³ has proposed the following method for the determination of proteids in animal matters. About 1 gram of the dried animal matter is washed with ether by decantation, using from 50 cc. to 100 cc. ether, and decanting through a filter which is to receive the portion insoluble in hot water. After allowing the ether to evaporate, the sample is washed by decantation, first with cold water and then with hot water, the total filtrate being from 300 cc. to 400 cc. The undissolved residues are brought on the filter with the last portions of water and the nitrogen in the residues determined by the Gunning-Kjeldahl method. The filtrate from the insoluble portions is received in Kjeldahl flasks, acidulated with 2 or 3 drops of strong hydrochloric acid, and then about 2 cc. of liquid bromine are added, and the contents of the flask shaken vigorously. Bromine is added until about 0.5 cc. remains undissolved and the supernatant liquid is thoroughly saturated. After standing over night, it is filtered and washed by decantation, the globule of bromine serving to saturate the wash-water. The filter with the precipitate is returned to the flask in which precipitation has taken place, and the nitrogen therein determined by the Gunning method.

METHOD MODIFIED.

After some experimentation the method above described was modified for vegetable materials as follows: 200 cc. of water were added to 1.4 grams of the substance in a Kjeldahl flask, heated to boiling, and allowed to cool. It was then acidified with hydrochloric acid, and bromine added until a small globule remained undissolved, the liquid allowed to stand over night,

¹ *Analyst*, 22, 228.

² *Ibid.*, 22, 258.

³ Bulletin 54, Division of Chemistry, U. S. Dept. of Agr.

filtered, and the precipitate washed by decantation, keeping the wash-water saturated with bromine. The filter and precipitate were returned to the flask, and the nitrogen therein determined by the Kjeldahl method.

COMPARISON OF THE BROMINE AND STUTZER METHOD.

Proteid nitrogen was determined in a number of materials by the method just described, and the results compared with those obtained by the Stutzer method. The following table contains the results:

Name of material.	Nitrogen. Stutzer method. Per cent.	Nitrogen. Bromine method. Per cent.
Corn silage.....	0.68	0.67
Crabgrass hay.....	1.38	1.51
Green peas.....	1.45	1.25
Cattail millet.....	1.34	1.10
Linseed meal.....	2.62	2.37
Corn bran.....	1.38	1.11
Wheat bran.....	1.79	1.51
Dried blood.....	13.00	12.53
Cowpea meal.....	3.19	2.53
Sheep excrement.....	2.79	2.13
Soy beans.....	5.97	5.23
Green rape.....	2.62	1.84

The bromine method is not applicable in the case of cottonseed meal. In one case the meal was extracted with water, and the extract gave a precipitate which settled almost immediately and contained 0.51 per cent. nitrogen. A duplicate determination gave a turbid liquid, which would not filter clear after standing over night, and when the precipitate finally settled it yielded only 0.10 per cent. nitrogen. When the meal was treated directly with bromine a turbid liquid was formed which refused to filter clear and the precipitate contained varying amounts of nitrogen. The results by the bromine method with two exceptions, are lower than with the Stutzer or the phosphotungstic acid methods. Until it has been proved that bromine precipitates all vegetable proteids quantitatively, which is doubtful, this method must be condemned.

THE STUTZER METHOD.

The Stutzer method used in this work is as follows: place 0.7

gram of the substance in a beaker, add 100 cc. water, heat to boiling, or, in case of substances rich in starch, heat on the water-bath ten minutes; add a quantity of copper hydroxide mixture containing about 0.5 gram of the hydroxide; stir thoroughly, filter when cold, wash with cold water and without removing the precipitate from the filter, determine nitrogen adding sufficient potassium sulphide solution to completely precipitate all copper and mercury. If the substance examined consists of seeds, or seed residues, or anything else rich in alkaline phosphates, add a few cubic centimeters of a concentrated solution of alum before adding the copper hydroxide and mix well by stirring.

Several objections have been made to this method. It has been stated¹ that, in some cases, working with a proteid alone, the copper compound underwent partial solution, a blue liquid being formed, although care had been taken to avoid the presence of free alkali. The proteids acting in this way were not named. Another objection has been founded on "the very slight solubility of the copper salts of some of the simpler amido-acids, especially leucin and glutamic acid; in a less degree the same statement applies to aspartic acid. Even at the temperature of boiling water the copper compounds of these substances are but very sparingly soluble, and if the liquid after digestion with cupric hydroxide, be filtered cold,² the compounds in question will, if present, be almost certainly left on the filter along with the proteid material."

Laszczyński³ also states that copper hydroxide precipitates the albumen of wort and beer completely, but also partly precipitates the albumoses and amides.

The copper salt of leucin is soluble in 3,045 parts of cold water and 1,460 parts of boiling water (Beilstein). When 0.7 gram of the substance and 100 cc. of water are used, for any of this salt to remain on the filter, 0.033 gram must be present, or 0.026 gram of leucin (since it contains 19.5 per cent. copper) which would be 3.7 per cent. The copper salt of glutamic acid is soluble in 3,400 parts of cold water and 400 parts of boiling water, and 0.029 gram must be present before any will separate

¹ Bulletin 54, Division of Chemistry, U. S. Dept. of Agr.

² Bulletin 46, Division of Chemistry, U. S. Dept. of Agr. (1895), p. 25.

³ *Analyst* (Abs.), 24, 184.

from 100 cc. water, equal to 0.022 gram glutamic acid, or 3.1 per cent. The solvent action of wash-water is left out of consideration.

When the material contains less than 3.7 per cent. leucin, or 3.1 per cent. of glutamic acid, there is no danger of the amide separating in the cold. But the limits are much higher than these. The solubilities above noted are for the pure salts in pure water. E. Schulze¹ emphasizes the fact that the copper salts of these amides are much more soluble when impurities are present. While the copper salts of aspartic acid and glutamic acid separate quickly from a pure solution, from a mixture of the two they separate very slowly, or not until the liquid has been evaporated.

It is probably better, however, to conduct the determination in a hot solution.

It has also been objected to this method, that albumoses are not precipitated. This objection might be overcome by the use of tannic acid to precipitate them. The tannic acid should be used after the precipitation with copper hydroxide. It is only in rare cases that its use would be necessary. Qualitative tests with tannic acid were made on the filtrates from cottonseed meal, wheat bran, cowpea meal, corn bran, cattail millet, excrement from crabgrass hay, waste rape, excrement from waste rape, and corn silage. A small precipitate was formed in all cases except with cattail millet and corn silage. The precipitate from cowpea meal and corn bran dissolved when the liquid was heated, reappearing on cooling. A repetition of the experiment showed that the precipitate did not always appear with the same material. A determination of nitrogen in the precipitate from cottonseed meal gave 0.03 per cent.—practically none.

CONCLUSIONS.

Phosphotungstic acid does not precipitate proteids completely at 90° or 100°.

Phosphotungstic acid at 60° precipitates very nearly the same quantity of nitrogen (with vegetable materials) as copper hydroxide.

Extraction of proteids with hot water does not always give concordant results.

¹ *Landw. Versuch.-Stat.*, 6, 220 (1886).

Bromine is not a suitable precipitant for proteids in vegetable materials.

The Stutzer method seems to be the method open to the fewest objections.

Acknowledgment is due Mr. H. W. Primrose, formerly assistant chemist, for assistance in the analytical work.

The above investigation was carried out in the laboratory of the North Carolina Agricultural Experiment Station with the permission of Professor W. A. Withers, chemist.

DETERMINATION OF CARBON IN FERROCHROME.

BY A. A. BLAIR.

Received August 14, 1900.

THE method in general use for the determination of carbon in ferrochrome may be briefly described as follows: Place 1 gram of the finely ground ferrochrome in a porcelain or platinum boat with 25 grams of fused potassium bisulphate and insert the boat in a porcelain tube in a gas furnace. Fit each end of the tube with a rubber stopper carrying a glass tube, and fill the forward part of the tube with lumps of cupric oxide. Connect the tube in the forward stopper with a U-tube containing strong sulphuric acid and chromic acid, a second U-tube containing dry pumice, a third containing dried, not fused, calcium chloride, the weighed absorption apparatus, and a guard tube. Connect the tube in the rear stopper with sources of purified oxygen and air. Start the oxygen through the apparatus and heat the tube carefully, beginning at the forward end which contains the oxide of copper, until the entire length of the tube inside the furnace is at a dull red heat in order to fuse the contents of the boat. Replace the oxygen with air, detach and weigh the absorption apparatus.

This does not seem very troublesome, but in practice several difficulties arise that make the method not only unsatisfactory, but very unreliable.

The sulphuric acid, both that evolved from the potassium bisulphate as sulphuric acid, and that evolved as sulphurous acid and oxidized to sulphuric acid by the oxide of copper and oxygen, acts on the rubber stoppers and sometimes carbonizes them

sufficiently to give results several times greater than the actual carbon content of the ferrochrome. The spattering of the bisulphate, no matter how carefully the heat is applied, generally covers the inside of the tube around the boat and cements boat and tube together. The absorption of sulphuric acid by the oxide of copper causes the latter to swell, usually breaking the tube in the second, and sometimes while it is cooling, in the first determination.

To avoid these difficulties and sources of error, I have devised the apparatus shown in the cuts.

Fig. 1 shows the platinum boats and cover. The smaller

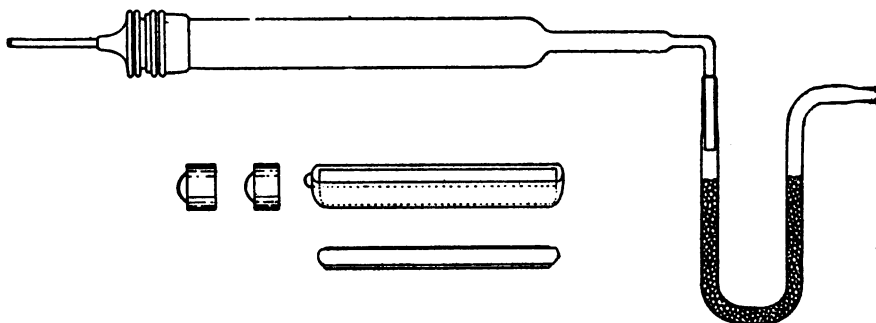
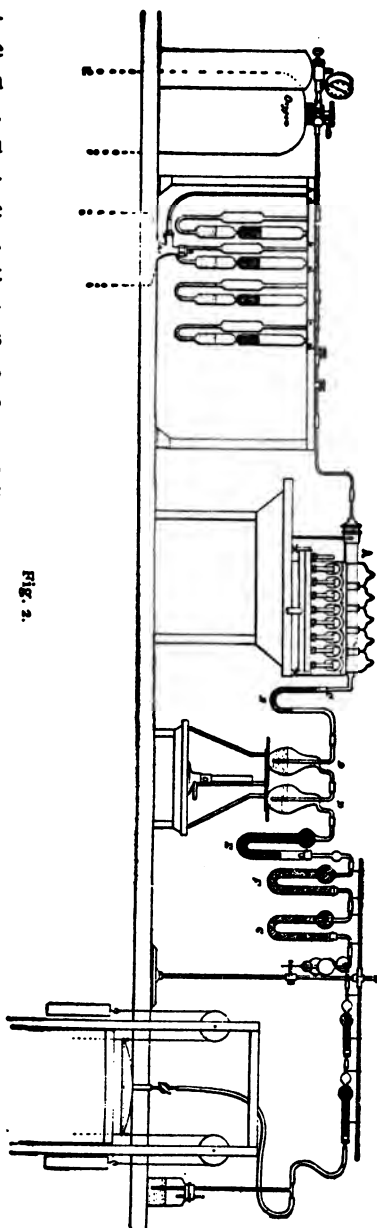


Fig. 1.

boat, 150 mm. long and 25 mm. wide, fits inside the larger and the cover is so arranged that any particles from the melting mass thrown on it run into the larger boat and thus keeps the tube itself perfectly clean.

The platinum tube, shown also in Fig. 1, is 400 mm. long and 30 mm. in diameter and is closed with a ground joint at the rear. The forward end for a distance of 75 mm. is contracted to 12 mm. and filled with platinized asbestos. It is then further contracted to 6 mm. in diameter, and a piece of glass tubing filled with glass beads is fused to it after it is bent downwards at an angle of 90° . The platinized asbestos facilitates the oxidation of the sulphurous acid evolved from the fused mass. The plugs are made of pumice wrapped with platinum foil, and are pushed in after the boat. They serve to fill the back end of the tube and prevent the diffusion of the evolved gases and consequent condensation of sulphuric acid around the ground joint.

Fig. 2 shows the general arrangement of the apparatus. The purifying apparatus for oxygen and air is shown in detail in Fig. 3. The tubes A and B contain respectively potassium hydroxide and concentrated sulphuric acid. It is almost impossible with this form of tube to throw out the contained liquid either forward or backward. In Fig. 2, A is the platinum tube, and B the glass tube containing beads fused to the contracted end of the platinum tube at C. D, D are glass flasks containing a solution of 150 grams of chromic acid and 300 cc. of strong sulphuric acid to the liter. These flasks stand on a copper plate and are heated by a Bunsen burner. The solution serves to oxidize any sulphurous acid that may have escaped oxidation in the contracted part of the platinum tube. E is a U-tube filled with glass beads, and acts as a condenser; F contains pumice saturated with chromic acid, and G contains dried calcium chloride. The absorption apparatus and guard tube follow. The latter is connected by a rubber tube with the gasometer, shown in the cut, which acts as an aspirator and serves to relieve the pressure in the apparatus, which, on account of the condensation of strong sulphuric acid in the tube B and the high spe-



cific gravity of the liquid in the flasks D, D, would otherwise be excessive. The details of this connection are shown in Fig. 4.

The method is as follows: Place 25 grams of pure potassium bisulphate in the small boat (Fig. 1), and fuse it over a Bunsen burner or blast-lamp to destroy any carbonaceous matter and allow it to cool. When cold spread 1 gram of the finely ground sample evenly over the surface of the fused mass, place the boat

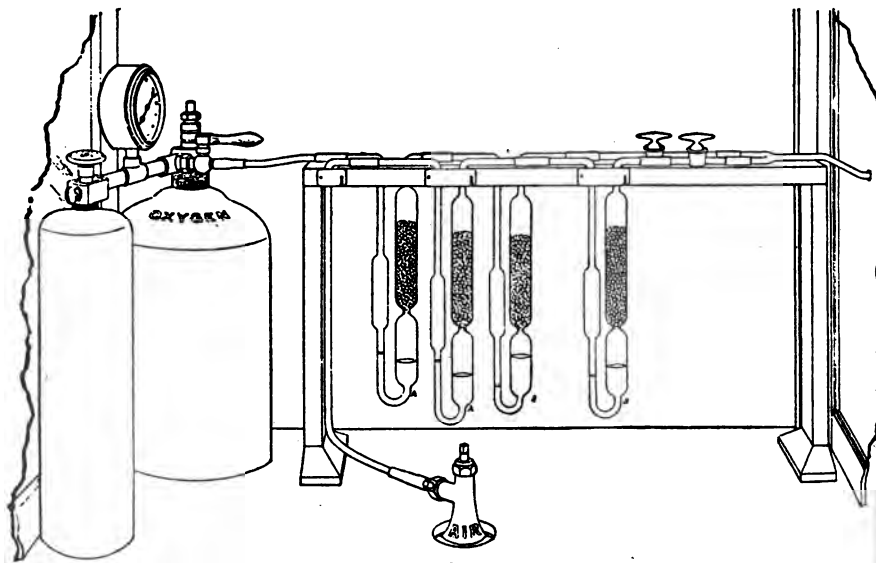


Fig. 3.

inside the larger boat, arrange the cover, place the boats in the tube, insert the plugs and close the tube with the ground joint. Connect the apparatus as shown in Fig. 3, and start a slow current of oxygen through the apparatus. Light the burners under the forward end of the tube which contains the platinized asbestos, and when this is red hot light the burner under the forward end of the boat and light the others successively until the tube is red hot for its entire length where the boat rests. Keep the tube hot for twenty minutes, replace the oxygen with air, turn out the lights, allow the air to run about thirty minutes and detach and weigh the absorption apparatus with the usual precautions.

As a large amount of sulphurous acid is produced it is neces-

sary to heat the tube very gradually in order to keep an excess of oxygen in the tube to oxidize all the sulphurous acid. As the sulphuric anhydride does not condense readily, a slow cur-

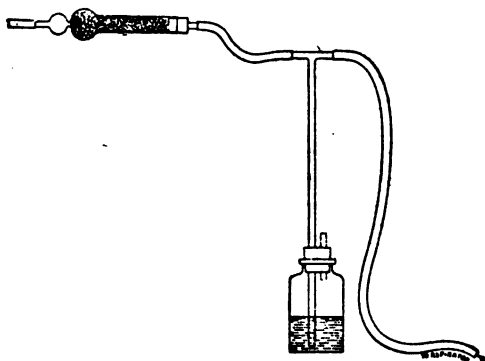


Fig. 4.

rent of gas is requisite, and a combustion requires about two hours and a half.

At the end of the operation the tube is opened and the plugs and boats removed. The fused mass is readily removed from the boats which, with the cover, are washed and ignited, ready for another combustion. About three determinations can be made in a day. Duplicate determinations agree within 0.01 per cent.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 51.]

THE ELECTROLYTIC OXIDATION OF TOLUENE.

By AARON MERZBACHER AND EDGAR F. SMITH.

Received September 7, 1900.

THE oxidation of toluene by electrolytic oxygen has been tried by Jos. H. James.¹ The products were a minute quantity of liquid, with an ester-like odor, and a resin, together with unaltered toluene.

Our attention has been attracted to this interesting subject and we have repeated the experiments, varying the conditions, of course, with the hope of finally changing the methyl side-chain to carboxyl.

The apparatus used in the electrolysis was similar to that

¹ This Journal, 21, 890.

generally employed in electrolytic oxidations: a large beaker glass in which stood a porous cup containing the anode liquor, and separating it from the cathode liquor. The porous cup was provided with a rubber stopper, carrying a condenser. The cathode liquor was either a 15 per cent. acid or alkali solution. Ordinary alcohol served as solvent for the toluene.

Experiment 1.—The conditions were as follows:

Toluene	10 grams.
Concentrated sulphuric acid	5 cc.
Water	50 cc.
Alcohol	150 cc.
N.D. ₁₀₀	1.1 A.
Volts	3.7
Temperature	40° C.
Time	7 hours.

As the action progressed the liquor assumed a dark yellow color. Upon examination, at the expiration of the oxidation period, unaltered toluene and a little resin were found present.

Experiment 2.—Acetone was substituted for the alcohol and the conditions were:

Toluene	10 grams.
Concentrated sulphuric acid	5 cc.
Water	75 cc.
Acetone	175 cc.
N.D. ₁₀₀	1.1 A.
Volts	3.5
Temperature	35°
Time	6 hours.

The anode liquor was carefully searched for new products: toluene and a little resin represented all that could be discovered.

Experiment 3.—An alkaline liquor was substituted for the acid of the two preceding experiments. The conditions were:

Toluene	10 grams.
Alcohol	110 cc.
Water	50 cc.
Sodium carbonate	5 grams.
N.D. ₁₀₀	0.54 A.
Volts	14
Temperature	40° C.
Time	3 hours.

Carbon dioxide was conducted through the cathode liquor

during the experiment. Very little of the toluene was changed. Resin was formed but nothing definite could be extracted from it.

Experiment 4.—A return to an acid solution will be observed in this experiment. Larger quantities of material were also used. The conditions were:

Toluene	55 grams.
Alcohol	190 cc.
Concentrated sulphuric acid	15 cc.
Water	15 cc.
N.D. ₁₀₀	1.1–1.6 A.
Volts	5–26
Temperature	20°–33° C.
Time	12 hours.

The anode liquor had the odor of benzaldehyde, and apparently that of ethyl benzoate. Three grams of resin were obtained. The fraction, boiling at about 213° C., was saponified with caustic potash, and the solution acidified with hydrochloric acid. The product, which separated, was recrystallized from ether. It melted at 121° C., and showed the characteristic tests of benzoic acid. The oxidation of toluene to benzoic acid had, therefore, really taken place, but in the presence of sulphuric acid and alcohol, ethyl benzoate (b. p. 213°) was formed. The quantity of the latter was not very great. The oxidation was far from being quantitative.

Another fraction, obtained from the anode liquor, boiled at 110°–190°. Phenylhydrazine was added to it. The hydrazone, which separated, was purified, when it melted at 150°, the melting-point of the hydrazone of benzaldehyde.

Additional experiments were made; the products were *resin*, *benzaldehyde*, and *ethyl benzoate*. The tests for the last two bodies were unmistakable. The gases evolved in these oxidations were carbon dioxide and oxygen.

The oxidation of ethyl benzene, under conditions similar to those last mentioned for toluene, gave some resin, ethyl benzoate, benzaldehyde, and a small fraction containing an aldehyde other than the latter, but in such slight amount that it could not be definitely identified.

It is proposed to attempt the electrolytic oxidation of the xylenes and of mesitylene.

[CONTRIBUTION FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

LECTURE EXPERIMENTS ILLUSTRATING THE ELECTROLYTIC DISSOCIATION THEORY AND THE LAWS OF THE VELOCITY AND EQUILIBRIUM OF CHEMICAL CHANGE.

BY A. A. NOYES AND A. A. BLANCHARD.

Received September 20, 1900.

INTRODUCTION.

THE experiments to be described in this paper were originally devised as an accompaniment to an extended course of lectures on theoretical chemistry.¹ Most of the principles illustrated are, however, of such fundamental importance that they must soon be generally introduced even into elementary lecture courses on inorganic and analytical chemistry; and it is the hope of the authors that this series of experiments will not only be of assistance to teachers of theoretical chemistry, but will also serve in some degree to hasten and facilitate the introduction of instruction in the principles of chemical equilibrium and of electrolytic dissociation into the elementary courses.

A few lecture experiments of a somewhat similar character have been previously published. Those of Küster,² and of Lash Miller and Kenrick,³ may be specially referred to.

The experiments are presented below in the form believed to be most convenient for those desiring actually to perform them. They are described in great detail, with the hope of saving others the large amount of time which has been expended in the attempt to find the best conditions for rapid and effective lecture demonstrations. It is, nevertheless, true that a slight accidental variation in one of the conditions, such as the dimensions of the apparatus employed, the temperature, or the concentration of the substances, may make modifications necessary; it is, therefore, of course, advisable to try the experiments before the lecture.

¹ Many of these experiments were shown in a lecture on "Some Applications of the Electrolytic Dissociation Theory" given before the American Chemical Society at its Columbus Meeting.

² *Ztschr. Electrochem.*, 4, 105.

³ This Journal, 22, 291-300; See also Jones and Allen: *Am. Chem. J.*, 18, 377; and Stieglitz: *Ibid.*, 23, 404.

The principles illustrated have been stated as briefly as possible in a non-mathematical form: in spite of the familiarity of these principles, it has seemed desirable to state them explicitly, in order to make clear the exact significance of each experiment.

PART I.—ELECTROLYTIC DISSOCIATION.

EXPERIMENT I.

Principle Illustrated.—The physical properties of dilute aqueous salt solutions are additive, being dependent on the nature of the metal and of the acid component of the salt, but not on their mutual relations. Since most salts in moderately dilute aqueous solution are, according to the dissociation theory, almost completely dissociated into their ions, all properties of such solutions must be the resultant of the properties of the solvent and of the separate ions, each ion having a definite influence which is independent of the nature of the other ion simultaneously present and of that of the undissociated salt from which it originated. This principle is best illustrated in the case where one of the ions has a characteristic property, such as color, not possessed at all by the other ion. Thus, all the salts of a metal whose ion is colored must have the same color in dilute aqueous solution, provided the negative ion of the salt is colorless, however different may be the colors of the undissociated salts. The colors of the latter may be shown, either in the solid state, or in a concentrated alcoholic solution.

Preparation of the Experiment.—Dissolve 60 grams of powdered $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 73 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ each in 100 cc. of alcohol, thus making a fivefold normal solution of each salt. Dissolve 27 grams of anhydrous cupric chloride (made by heating the blue crystals in a porcelain dish over a free flame) and 48 grams of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, each in 100 cc. of absolute alcohol, thus making a fourfold normal solution of each salt. Pass into the cupric chloride solution a few cubic centimeters of dry hydrochloric acid gas. Place 20 cc. of each of these solutions in four large test-tubes. Provide also distilled water, concentrated ammonia, and 20 cc. of concentrated potassium cyanide solution.

Experiment.—Add 100 cc. of cold water to each of the four solutions. Then add 20 cc. of ammonia to one of the copper

solutions, and 20 cc. of concentrated potassium cyanide solution to one of the cobalt solutions.

Observations.—The alcoholic solutions of cobalt chloride and nitrate are deep violet-blue and purplish red, respectively, but become of the same shade of pink after dilution with water. Those of copper chloride and nitrate are originally greenish black and light blue, respectively, but become of the same shade of blue on dilution. The ammonia added to the copper solution produces a much more intense blue coloration of a different shade, and the potassium cyanide added to the cobalt solution changes its color from pink to brown.

Remarks.—The hydrochloric acid gas is passed into the cupric chloride solution in order to avoid the precipitation of a basic salt on subsequent dilution.

The change in color accompanying the dilution may well be due mainly to hydration of the salts rather than to dissociation of them; but whatever the cause, the experiment evidently still illustrates the principle of the dependence of the properties of dilute aqueous solutions on those of the separate ions. The addition of ammonia to the copper solution transforms the copper ions into complex positive ions of the form $\text{Cu}(\text{NH}_3)_4^+$; and that of potassium cyanide to the cobalt solution converts the cobalt ions into complex negative ions, probably of the composition, $\text{Co}(\text{CN})_6^-$. These explanations show that the exceptions to the principle of additivity which are illustrated by the last part of the experiment are in full accord with the dissociation theory; for the nature of the ions having changed, the color of the solution must change likewise.

EXPERIMENT II.

Principle Illustrated.—Metathetical reactions between dissolved salts take place instantaneously, whatever may be the nature of the salts, while those in which organic compounds are involved commonly require an appreciable time which varies greatly with the nature of the compound. This difference of behavior is, according to the dissociation theory, due to the fact that the ions of salts, being already separated by the solvent, are capable of immediate combination, when those which have the tendency to combine are brought into contact, while the component elements

or radicals of organic substances must be separated from each other before they can enter into a metathesis. A very slight degree of dissociation of the salts is sufficient, however, owing to the fact that the ions removed by the metathesis are immediately replaced by others by the spontaneous and almost instantaneous process of dissociation.

Preparation.—Prepare 100 cc. of nearly saturated solution of potassium bromide and of zinc bromide in alcohol, and equal quantities of 5 per cent. solutions of isopropyl bromide, ethyl bromide, and phenyl bromide. Place these solutions in five lecture jars. Prepare 150 cc. of a nearly saturated alcoholic solution of silver nitrate (about 25 grams to the liter). Provide a stirring rod with one end flattened at right angles to the rod, for vertical stirring.

Experiment.—Add 20 cc. of the alcoholic silver nitrate solution to each of the five bromide solutions and stir.

Observations.—The potassium and zinc bromide solutions both give instantly with the silver nitrate a copious flocculent precipitate. The isopropyl bromide solution becomes turbid immediately, but an appreciable time is seen to be required for the completion of the precipitation. The ethyl bromide remains clear for a few seconds, and then becomes turbid, but the turbidity increases very slowly on standing. The phenyl bromide gives no turbidity, even after long standing.

Remarks.—Care must be taken that the ethyl and phenyl bromides are free from hydrobromic acid and bromine. These impurities, if present, may be removed by washing in a separatory funnel, first with dilute sodium carbonate solution, and then with water.

EXPERIMENT III.

Principle Illustrated.—The passage of electricity through a salt solution causes the metallic component of the salt to move in the direction of the current, and the acid component to move in the opposite direction. The products into which salts in aqueous solution are dissociated are therefore electrically charged molecules or ions.

Preparation.—Cut 10 grams of agar-agar in small pieces, place in a casserole, add 500 cc. of cold water, heat to boiling,

and boil until a clear solution is formed. Strain while still hot through a piece of cloth, and preserve the jelly formed on cooling as a stock for use in this and the next two experiments. To 35 cc. of the remelted agar add 8 cc. of saturated cupric chloride solution, a few drops of acetic acid, and 6 cc. of saturated potassium bichromate solution. Pour enough of this solution into a U-tube 2 cm. in diameter and 16 cm. high to fill the tube 3-4 cm. above the bend, and allow the jelly to harden. Sprinkle on each surface a little bone-black to mark the boundary, then pour into each arm a few drops (to fix the bone-black in place) of a solution made by mixing 4 cc. of saturated potassium chloride solution with 15 cc. of the melted stock-agar, cool in water, and after a few moments pour in enough more of this mixture to form a layer a few centimeters high in each arm. After this has hardened, pour into each arm a few cubic centimeters of saturated potassium chloride solution, insert electrodes of platinum wire in both arms, and connect them through an open switch and a 32 candle-power 110-volt lamp with the terminals of a 110-volt direct-current circuit. Place the U-tube in a beaker of water containing a large quantity of ice.

Experiment.—Close the switch and allow the current to pass through the tube for ten to thirty minutes, stopping it temporarily if the agar should show signs of melting.

Observations.—The copper chromate jelly filling the bottom of the tube has a deep green color. After the current has passed for some minutes a blue zone (due to the copper ions) appears above the bone-black boundary in one arm, and a yellow zone (due to chromate ions) above the bone-black in the other arm, and these zones both extend upwards as the electrolysis continues. The zones immediately below the bone-black in both arms also acquire a blue and yellow color respectively, while the central portion beneath remains unchanged in color.

Remarks.—The experiment should be prepared not more than an hour or two before the lecture, as otherwise the boundaries will not be sharp, owing to diffusion. It is desirable to use, as directed, a larger proportion of copper salt than corresponds to the normal chromate, since otherwise the color of the blue copper zone will not be deep enough to be visible at a distance. The

acetic acid is added to prevent the precipitation of a basic chromate. The potassium chloride in the arms of the tube serves to form a colorless conducting layer, its ions carrying the current to and from the boundary of the copper chromate. Accurate experiments have shown that the addition of enough agar to form a solid jelly does not affect the rate of migration of the ions more than a few per cent.; there is, therefore, no objection to its use for purposes of demonstration.

EXPERIMENT IV.

Principle Illustrated.—The rate of migration of the ions is dependent on their nature. The hydrogen ion moves most rapidly, the hydroxyl ion about one-half as fast, and other inorganic ions from one-fourth to one-eighth as fast as the hydrogen ion. The rate of motion of the ions and the number of them present are the two factors determining the conductivity of a solution.

Preparation.—Fill the bend of a U-tube (2 cm. in diameter, and 16 cm. high) and one of its arms up to a point 5 cm. from the top with a jelly made of 16 cc. of saturated potassium chloride solution, 12 drops of phenolphthalein solution, 50 cc. of the stock-agar (see Expt. III), and just enough potassium hydroxide to color it deeply red. Fill the other arm of the tube up to 5 cm. from the top with some of the same jelly to which has been added just twice as much hydrochloric acid as is needed to decolorize it. Place platinum wires in the air spaces at the top of each arm, and connect these wires through a 32-candle-power 110-volt lamp with the terminals of a 110-volt direct-current circuit in such a manner that the current will enter the arm containing the colored jelly. Place the tube in a beaker of water containing pieces of ice. Prepare a mixture of 0.5 cc. of hydrochloric acid (sp. gr. 1.12), 6 cc. of saturated copper chloride, and 20 cc. of water, and a mixture of 2 cc. of 10 per cent. potassium hydroxide solution with 20 cc. of saturated potassium chloride solution.

Experiment.—Nearly fill the arm of the tube containing the colored jelly with the solution of copper chloride and hydrochloric acid and the other arm with the solution of potassium hydroxide

and chloride, close the switch, and allow the current (of about 0.5 ampere) to pass for about fifteen minutes.

Observations.—A colorless zone (due to the hydrogen ions) descends into the pink jelly to a depth of about $5\frac{1}{2}$ cm., and this is followed by a blue zone (due to the copper ions) to a depth of 1 cm. In the other arm a pink zone (due to the hydroxyl ions) descends into the colorless jelly to a depth of about $2\frac{1}{2}$ cm.

EXPERIMENT V.

Principle Illustrated.—The composition of the ions can be determined by migration experiments. Thus in the case of the double cyanide of potassium and silver, the silver can be shown to move against the current, thus proving that it forms a part of the negative ion, which has in fact been shown to have the composition $\text{Ag}(\text{CN})_2$.

Preparation.—Charge a U-tube, 2 cm. in diameter and 16 cm. high, not more than an hour or two before the experiment is to be performed, in the manner shown in the accompanying scale

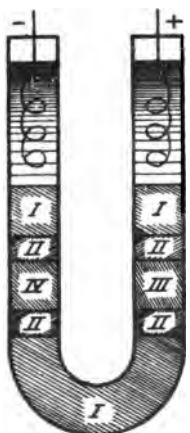


Fig. 1.

drawing, with various jellies, designated I, II, III, and IV. Jelly No. I, is prepared from 30 cc. of the stock-agar (Expt. No. III), 6 cc. of saturated potassium nitrate solution, and 6 cc. of a suspension of washed precipitated zinc sulphide in water; jelly No. II, from 15 cc. of the agar and 4 cc. of saturated potassium nitrate solution; jelly No. III, from 5 cc. of the agar, 1 cc. of saturated potassium nitrate, and 1 cc. of a 3 per cent. silver nitrate solution; and jelly No. IV, from 5 cc. of the agar, 1 cc. of saturated potassium nitrate solution, and 1 cc. of a potassium silver cyanide solution made by adding concentrated potassium cyanide solution, drop by drop, to a 3 per cent. silver nitrate solution until the precipitate first formed redissolves. In charging the tube, pour in each portion of melted jelly through a long-necked funnel to avoid contaminating succeeding portions, and cause each to harden by immersing in cold water before adding the next. Make each of the layers of a thickness corresponding to that shown in the drawing, taking especial care that the layers

of jelly II be not more than 1 cm. thick, since otherwise too long a time will be required for the experiment; and in forming the last layers, pour in first a few drops of the solution, allow this to solidify, and then add the remainder, in order to prevent them from taking up and mixing with any of the jelly beneath. Pour into each arm on top of the jelly some saturated potassium nitrate solution, insert platinum wires, and connect them with the terminals of a 110-volt direct-current circuit in such a manner that the current will enter the arm containing the silver nitrate jelly (No. III). Immerse the tube in a beaker of ice and water.

Experiment.—Cause the current (which will be one of about 0.35 ampere) to pass through the tube for fifteen to twenty minutes, stopping it temporarily or inserting additional resistance if the agar shows signs of melting.

Observations.—The zinc sulphide jelly at the bottom, which is pure white at first, after a few minutes begins to blacken at its surface below the silver nitrate, and a few minutes later at its other surface below the potassium silver cyanide, the blackening extending rapidly downward on both sides. The zinc sulphide layers near the top of the arms remain white throughout the experiment.

Remark.—Zinc sulphide is used instead of an alkaline sulphide to indicate the presence of silver, since, being nearly insoluble, it does not move appreciably with the current.

EXPERIMENT VI.

Principle Illustrated.—The molecular conductivity of salts increases on dilution at first rapidly, and then more slowly, and finally attains a constant maximum value which is not affected by further dilution. The molecular conductivity of a dissolved substance is the conductivity of that volume of its solution which contains 1 mol of the substance, when the solution is placed between parallel electrodes of sufficient extent, 1 cm. apart. According to the dissociation theory, the change of this property on dilution results from the fact that electricity is transported through the solution solely by the ions, and the number of these is increased at the expense of the undissociated portion of the salt by increased dilution, up to the point where the salt is com-

pletely dissociated, after which further dilution has, of course, no further effect.

Preparation.—Construct a high, narrow trough with parallel glass sides and wooden ends and base in the following manner : Cover one of the broad surfaces of each of two strips of wood 45 cm. long, 1 cm. thick, and 2.2 cm. wide, previously oiled and shellaced, with a strip of thin silver foil, attaching this to the wood by means of shellac. Insert these two strips of wood with the silver-covered surfaces towards each other and *uniformly* 18.5 cm. apart between two sheets of plate glass ($45 \times 22.5 \times 0.6$ cm.) so as to leave a free space about 1 cm. deep outside of the strips. Clamp the apparatus together temporarily, and fill this free space with a melted cement made by stirring one part of beeswax into five parts of melted rosin. Bind tightly over each of these two ends a piece of stout cloth or canvas, and attach it to the glass sides by means of shellac, so as to hold the whole in position. Insert this cell into a wooden base so made that the cell will fit tightly into a groove to a depth of 1.5 cm.; pour on to the bottom inside more of the above cement heated enough to be very fluid, and allow the cement to cool, so as to form an even horizontal layer. Solder wires to the tops of the silver electrodes. Connect the resistance cell thus constructed in series with a storage cell, a switch, and a suitable current indicator. Use as a current-indicator any Weston station voltmeter, from which the series resistance coil in the back has been removed or short circuited. (The moving coils in all the Weston station voltmeters have a resistance of about 75 ohms; and a full scale deflection is obtained with a current of about 0.012 ampere; the station type is used since it has a pointer which can easily be seen at a distance.) Prepare a stirring rod by closing up one end of a wide glass tube 0.6 meter long. Provide a glass siphon suitable for emptying the resistance cell, and fill it with water; also a funnel attached to a tube long enough to reach the bottom of the cell. Measure out in four graduates three portions of distilled water of 60, 240, and 960 cc., respectively. Prepare 20 cc. of a fourfold normal silver nitrate solution by dissolving 13.5 grams of solid silver nitrate in water, and making the volume up to 20 cc.

Experiment.—Fill the resistance cell with distilled water, and close the switch for a few moments. Insert the siphon, and empty the cell completely, tilting it at the end. Then pour into the bottom of the cell through the funnel the 20 cc. of fourfold normal silver nitrate solution. Close the switch, and note on the board the scale reading. Then pour into the cell the 60 cc. portion of water, stir, and note the reading. Then pour in successively the 240 cc. and the 960 cc. portions of water, noting the readings after the complete addition of each portion.

Observations.—A scarcely noticeable deflection of the needle is produced when the cell is filled with pure water. The scale-readings corresponding to the most concentrated solution and the first fourfold dilution of it are found to differ greatly, those of the first and second dilutions much less, and those of the second and third dilutions by only a relatively small amount; thus the scale-readings in an actual experiment were 7.1, 8.4, 9.2, and 9.5.

Remarks.—In the apparatus and experiment above described the distance between the electrodes, though not 1 cm., is a constant distance, and the amount of the salt used, though not 1 mol, is a definite amount, so that a satisfactory illustration is given of the property of molecular conductivity and of its variation with the dilution, a phenomenon, which, as is well known, was the starting-point of the electrolytic dissociation theory, and one which forms the basis of the most important method of determining dissociation.

The molecular conductivities of the silver nitrate solutions are at the four concentrations, according to Kohlrausch, approximately 39, 63, 80, and 92 units. The effect of having the resistance (about 75 ohms) of the voltmeter constantly in series with the cell is to make the apparent change of conductivity less than the true change; nevertheless, the effect is sufficiently great to make the demonstration an entirely satisfactory one, as is shown by the scale-readings cited above.

If copper electrodes are substituted for the silver ones, and a copper salt solution for the silver nitrate, the change of conductivity with the dilution is still greater; but the experiment is far less satisfactory, for it is not possible, owing to the great dilu-

tion required, to illustrate the approach to a maximum value.

EXPERIMENT VII.

Principle Illustrated.—Different acids of the same concentration differ greatly in their conductivities and degrees of dissociation; but their neutral salts have approximately the same conductivities and same degrees of dissociation.

Preparation.—Fill four 500 cc. bottles with half-normal solutions of hydrochloric acid, sulphuric acid, chloracetic acid, and acetic acid, prepared by weighing out the calculated amounts of the commercial acids. (It is desirable, however, to prove the approximate equivalence in the concentrations of the four acids by titration with normal potassium hydroxide, and to adjust them if they differ by more than five per cent.) Distinctly label these solutions, and reserve them for use in this and later experiments.

Make the apparatus represented in the accompanying figure in the following manner: Procure four glass tubes as nearly alike as possible, of an internal diameter of about 3 cm. and a length of 20 cm. (The straight parts of "student lamp" chimneys can be used for the purpose.) Place in one end of each of these tubes a rubber stopper with one hole in which has been inserted a small glass tube containing a stout copper wire to which a thin circular platinum disk is soldered, this disk covering the small end of the rubber stopper and being attached to it by means of sealing-wax. Set up the tubes in a vertical position with the stoppers at the bottom, holding the tubes in place by means of clamps or by a suitable wooden frame made for the purpose. Insert in the upper end of each of the tubes a rubber stopper carrying a small thick-walled glass tube 22 cm. long through which passes a stout copper wire, to the lower end of which is soldered, at right angles to the wire, a thin circular platinum disk of a diameter a few millimeters less than that of the tube, the disk being reinforced by a thick layer of sealing-wax on its upper surface. These tubes should move freely through the stoppers, but yet be held in place by them. Connect the wire issuing from the bottom of each large tube with a 32-candle-power 110-volt lamp placed in a socket beneath; make also the other connections shown in the drawing, using short coils of

covered flexible wires between the four upper electrodes; and finally, connect through an open switch the upper electrodes with one terminal and the lamps with the other terminal of a

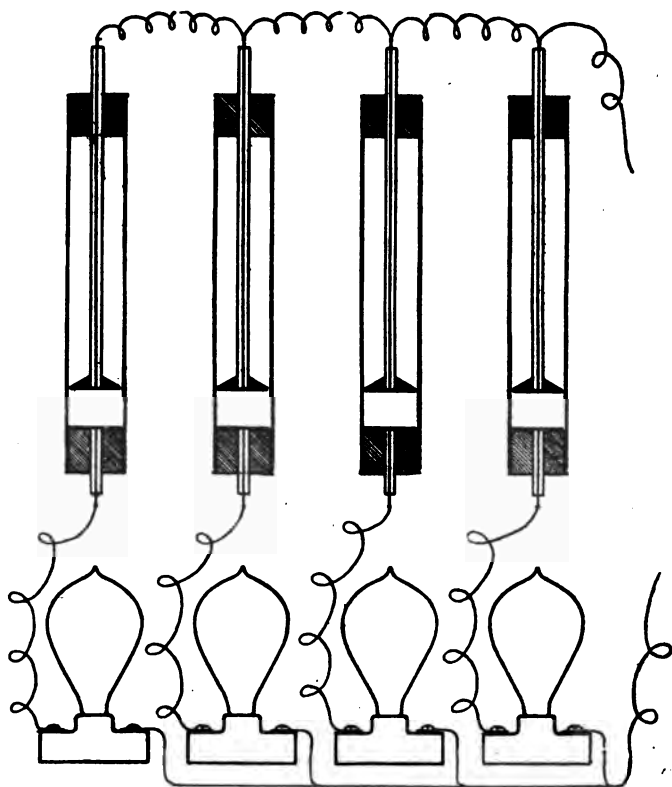


Fig. 2.

110-volt alternating circuit. Place in each tube 120 cc. of distilled water and set the electrodes one-third of the distance from the bottom. Provide a 5 cc. graduated pipette, a little phenolphthalein solution, and 50 cc. of normal potassium hydroxide solution.

Experiment.—Raise the stoppers carrying the upper electrodes, and add to each of the four tubes with the pipette 5 cc. of each of the four half-normal acids, so that they will be in the order, acetic, chloracetic, sulphuric, hydrochloric, and stir thoroughly. Re-insert the electrodes, darken the room somewhat, and close

the circuit. Raise the electrode in the hydrochloric acid solution to the top of the tube, and then adjust the heights of the other three electrodes so that all the lamps beneath glow with equal brilliancy. Admit the light to the room, and call attention to the relative heights of the four electrodes. Then raise the stoppers, and add to each tube two or three drops of phenolphthalein solution and from the pipette about 2.5 cc. of a normal solution of pure potassium hydroxide, adding the last few drops in each case slowly and with vigorous stirring, until the solution remains permanently colored. Again darken the room, set the electrode in the potassium chloride solution about one-third of the total distance from the bottom, and adjust the other three electrodes so that all four lamps glow with equal brilliancy. Admit the light to the room, and call attention to the heights of the four electrodes.

Observations.—Starting as directed with the four electrodes at the same height, about one-third of the distance from the bottom, it is seen when the circuit is closed that the lamps are more brilliant in correspondence with the order, hydrochloric, sulphuric, chloracetic, acetic, the lamp beneath the last-named acid not glowing perceptibly. After the lamps are brought to equal brilliancy by adjusting the electrodes, it is seen that if the upper electrode in the hydrochloric acid is at the top, that in the sulphuric acid is about one-fourth of the distance down, that in the chloracetic acid three-fourths of the distance down, and that in the acetic acid nearly touching the lower electrode. It is seen that nearly equal amounts of potassium hydroxide are required for the neutralization of all four acids, thus proving them of equal concentration. Finally after adjusting the lamps to constant brilliancy, the electrodes in the salt solutions are seen to stand at not far from the same heights.

Remarks.—The chloracetic acid solution must be prepared not more than a few days before it is used, since, otherwise, it will contain an appreciable amount of hydrochloric acid. If an alternating circuit is not available, a direct circuit may be used, but in that case it is desirable that the upper electrodes be made convex downwards so that the gas will escape, and that the circuit be closed only for as short a time as is necessary.

Instead of charging the tubes of the conductivity apparatus during the lecture with the acids, this may be done beforehand, in order to save time; but in that case, the audience is obliged to take for granted the fact that the acids used in the later experiments are identical with those used in this one, a fact which is made obvious if the portions of acids are in each case drawn from the same bottles. In fact, throughout most of the following experiments, much time can be saved in the lecture by measuring out the solutions in advance, the audience being asked to accept the lecturer's statement in regard to their composition. While the purpose of such experiments is to illustrate rather than to demonstrate, it is nevertheless true that they become less satisfactory, the more the audience has to take for granted. To what extent it is desirable to carry the preparation of the experiments, will therefore depend on the character of the lectures, on the time that can be given to experiments, and whether the services of an assistant are available during the lecture.

Lecturers will, we believe, find themselves repaid for the small amount of labor involved in the construction of the apparatus just described; for not only is the above experiment a very satisfactory one, but the same apparatus can be employed for the demonstration of Ostwald's dilution law (see Expt. XII), and for the illustration of the conductivity and dissociation of many substances besides those here used. It should be stated that the apparatus was devised and first constructed by Dr. W. R. Whitney of our Institute.

PART II.—THE VELOCITY OF CHEMICAL REACTIONS.

EXPERIMENT VIII.

Principle Illustrated.—The rate at which a chemical change takes place is proportional to the concentration of each of the substances taking part in it.¹

Preparation.—In a 2-liter bottle put 1600 cc. of distilled water, 50 cc. of half-normal hydrochloric acid, and 40 cc. of starch solution (made by rubbing 1 gram of potato starch to a paste with

¹ As is well known, the rate is in some cases proportional to that power of the concentration which corresponds to the number of molecules involved; but this experiment illustrates only the simpler case—

5 cc. of cold water, pouring 150 cc. of boiling water over it, allowing the undissolved part to settle, and decanting the supernatant liquid). Prepare a 0.5 normal solution of potassium bromate by dissolving 7 grams of the salt in half a liter of water; also a 0.5 normal solution of potassium iodide by dissolving 42 grams of it in half a liter of water. Reserve these solutions for use in the three following experiments: Provide four 500 cc. white glass stoppered bottles, 8 cm. in diameter, and set two 10 cc. graduates in front of each of them. Prepare a standard blue solution in a fifth 500 cc. bottle by adding to 400 cc. of water, 10 cc. of the starch solution and 1 cc. of a solution of 1 gram of iodine and 2 grams of potassium iodide in 500 cc. of water. Place all five bottles on the lecture table against a background of white paper. Provide a large clock (or stop-watch) with a second hand; also a 500 cc. graduate.

Experiment.—Pour into each of the four bottles from the large graduate 400 cc. of the acid solution in the 2-liter bottle. Pour into the four pairs of 10 cc. graduates respectively 5 cc. of the bromate and 5 cc. of the iodide solution, 10 cc. bromate and 5 cc. iodide, 5 cc. bromate and 10 cc. iodide, and 10 cc. bromate and 10 cc. iodide. Add to each of the four bottles the bromate solution from the graduate before it, and then, at a definite instant, when the second hand of the clock shows an even minute, add simultaneously to the four bottles the measured portions of iodide solution, quickly insert the stoppers, and shake vigorously. Note on the board by reference to the clock the times when each of the solutions becomes of the same shade of blue as the standard, placing the latter in succession by the side of the different reaction bottles.

Observations.—The mixture containing the 10 cc. of both bromate and iodide will become of the same shade of blue as the standard in about thirty seconds. The mixtures with 10 cc. bromate and 5 cc. iodide and with 5 cc. bromate and 10 cc. iodide will both require the same interval of time, which will be about twice as great as that for the first mixture. The mixture containing 5 cc. of both bromate and iodide will require nearly twice as much time as these last mixtures.

EXPERIMENT IX.

Principle Illustrated.—Equal increments of temperature cause an equal multiplication of the velocity of any definite chemical reaction.¹

Preparation.—Mix in a 2-liter bottle 1100 cc. of water, 100 cc. of 0.5 normal hydrochloric acid, and 30 cc. of starch solution. Put 400 cc. of this solution into each of three 500 cc. white glass-stoppered bottles (8 cm. in diameter) ; bring by means of suitable baths one of these solutions to 4°, another to 16°, and the third to 28° ; and allow the bottles to stand in the baths until the experiment is to be shown. Mix in a 50 cc. graduate 10 cc. of 0.5 normal potassium bromate, 10 cc. of 0.5 normal potassium iodide, and 25 cc. of water, all measured as closely as possible ; and pour just 10 cc. of this mixture into each of three 10 cc. graduates. Provide a clock with a second hand, and a large thermometer of short range whose readings are visible at a distance. Prepare in a fourth bottle, just as in Expt. VIII, a blue iodide of starch solution to serve as a standard. Place all four bottles against a background of white paper.

Experiment.—Insert the thermometer in succession in each of the three bottles, and note the temperatures on the board. At a definite instant, when the clock shows an even minute or half minute, pour the three portions of bromate solution into the three bottles, stopper quickly, and shake vigorously. Note on the board the times at which the three solutions reach the same depth of blue as the standard.

Observations.—The times required to reach the color of the standard will be about thirty-two seconds, fifty-eight seconds, and one hundred and five seconds at 28°, 16°, and 4°, respectively.

Remarks.—The hottest solution must not be above 30°, since otherwise a considerable error arises from the lessening of the depth of color of the iodide of starch. Between 4° and 30°, however, the intensity of color undergoes a scarcely perceptible change, as was proved by a special experiment.

EXPERIMENT X.

Principle Illustrated.—The effect of acids in accelerating chem-

¹ This principle may be somewhat more explicitly stated as follows : In the case of any chemical reaction, the velocity-coefficients corresponding to an arithmetical series of temperatures, form a geometrical series.

ical reactions is roughly proportional to their electrical conductivities. The effect is primarily dependent on the hydrogen ions, and is in most cases approximately proportional to their concentration.¹

Preparation.—Mix in a 2 liter bottle, 40 cc. of 0.5 normal potassium iodide, 40 cc. of 0.5 normal potassium bromate, 40 cc. of starch solution, and 1600 cc. of water. Place on the lecture table the four half-normal solutions used in Expt. VII, four 500 cc. bottles, four 10 cc. graduates, a 500 cc. graduate, and white paper arranged so as to serve as a background.

Experiment.—Measure with the large graduate 400 cc. of the bromate-iodide mixture into each of the four bottles. Pour into the small graduates just 10 cc. of each of the half-normal acids, and place them in front of the four bottles in the order hydrochloric, sulphuric, chloracetic, acetic acid. Add at the same instant the contents of the four graduates to the bottles, stopper quickly, and shake.

Observations.—The solution containing the hydrochloric acid becomes deep blue almost immediately; that with the sulphuric acid, within half a minute; that with the chloracetic acid, after three or four minutes; and that with acetic acid, only after three or four hours.

EXPERIMENT XI.

Principle Illustrated.—Neutral substances sometimes act as powerful catalytic agents.

Preparation.—Place in a liter bottle 800 cc. of water, 40 cc. of 0.5 normal potassium iodide, 40 cc. of 0.5 normal potassium bromate, and 20 cc. of starch solution. Provide a half-normal solution of acetic acid and a neutral saturated solution of ferrous sulphate; also, a graduated 1 cc. pipette, two 500 cc. bottles, and two 50 cc. and one 500 cc. graduates.

Experiment.—Measure into each of the two bottles, with the large graduate, 400 cc. of the bromate-iodide mixture. Measure out in each of the two graduates 50 cc. of the half-normal acetic acid, and add to one of the graduates 0.5 cc. of the ferrous sul-

¹ In the case of the bromate-iodide reaction the accelerating effect increases much more rapidly than the concentration of the hydrogen ions (see *Ztschr. phys. Chem.*, 19, 599); but in spite of this exceptional behavior, it can be used to demonstrate the order of the effect of different acids, which is all that is attempted in this experiment.

phate solution. At the same moment add the contents of the graduates to the two bottles, quickly insert the stoppers, and shake.

Observations.—The solution containing the ferrous sulphate becomes deep blue within a few seconds, while that not containing it requires as many minutes to reach the same depth of color.

PART III.—CHEMICAL EQUILIBRIUM OF DISSOCIATED SUBSTANCES.

EXPERIMENT XII.

Principle Illustrated.—The molecular conductivity, and therefore the dissociation, of a slightly dissociated acid varies as the square root of the volume in which a definite quantity of the acid is contained, in accordance with the requirement of the mass action law. The general expression of the effect of dilution on the dissociation of acids, or of the so-called Ostwald's dilution law, is

$\frac{d^2}{(1-d)v} = K$, where d is the degree of dissociation, v the volume containing 1 molecule, and K the dissociation-constant. If d is small, the quantity $(1-d)$ can be considered equal to unity without great error, whence the above-stated principle follows.

Preparation.—Place on the lecture table the conductivity apparatus and the half-normal chloracetic acid solution used in Expt. VII. Provide two 300 cc. beakers and a 50 cc. and a 200 cc. graduate, also half a liter of distilled water and have this at the same temperature (that of the room) as the chloracetic acid. Connect the conductivity apparatus through a switch with the terminals of a 110-volt alternating circuit.

Experiment.—Mix in a beaker 50 cc. of the half-normal chloracetic acid solution with 150 cc. of water. In a second beaker dilute 50 cc. of the solution so obtained with 150 cc. of water. Nearly fill three of the tubes of the conductivity apparatus with the half-normal chloracetic acid from the bottle, and with the two diluted solutions in the beakers respectively. Raise the electrode in the tube containing the most concentrated acid to the top, darken the room, close the circuit, and adjust the other two electrodes so that the three lamps beneath glow with equal brilliancy.

Open the circuit, admit the light, and call attention to the position of the electrodes.

Observations.—At the close of the experiment it is seen that the electrodes in the half-normal solution are about twice as far apart as those in the eighth-normal solution, and about four times as far apart as those in the $1/32$ -normal.

Remarks.—The remark on Expt. VII in regard to the use of a direct current applies here also.

The distances between the electrodes are directly proportional to the specific conductivities of the solutions; consequently, the molecular conductivities are proportional to the products of these distances into the volumes in which a definite amount of acid is contained.

Chloracetic acid is 5.4, 10.5, and 20.0 per cent. dissociated in $1/2$, $1/8$, and $1/32$ -normal solutions respectively. Owing to the rather large degree of dissociation, the proportionality between this and the square root of the volume is not exact; but the deviations are not great enough to be noticeable in the experiment here described.

EXPERIMENT XIII.

Principle Illustrated.—The dissociation of a slightly dissociated acid (or base) is very greatly reduced by the addition of an equivalent quantity of one of its neutral salts. For, according to the mass action law, the product of the concentrations of the two ions of the acid is proportional to the concentration of its undissociated portion, and since the concentration of the negative ion is largely increased by the addition of the neutral salt, the ratio of the concentration of the hydrogen ion to that of the undissociated acid must decrease in the same proportion. In the following experiment, in order to show the difference in the concentrations of the hydrogen ion in the two cases, use is made of the relative effects of the acid, in the absence and presence of its neutral salt, in accelerating the bromate-iodide reaction.

Preparation.—In a liter bottle place 700 cc. of distilled water, 20 cc. of 0.5-normal potassium bromate, 20 cc. of 0.5-normal potassium iodide, and 10 cc. of starch solution. Place on the lecture table the half-normal solution of chloracetic acid and a normal one of potassium hydroxide; also a 500 cc. graduate,

two 100 cc. graduates, a 200 cc. beaker, two 500 cc. bottles, a phenolphthalein solution, and some distilled water.

Experiment.—Measure with the large graduate, 350 cc. of the bromate-iodide mixture into each of the 500 cc. bottles. Measure out 40 cc. of chloracetic acid into each of the two 100 cc. graduates. To one graduate add 60 cc. of water, and mix by stoppering the graduate and shaking. Pour the contents of the other graduate into the beaker, add a few drops of phenolphthalein and about 20 cc. of the normal potassium hydroxide solution, adding the last portion slowly with stirring so as to attain closely the neutral point; then add 40 cc. more of the chloracetic acid solution and pour the mixture back into the graduate. At the same moment add the contents of the two graduates to the two bottles containing the bromate-iodide mixture, insert the stoppers, and shake vigorously.

Observations.—The blue color appears very quickly in the bottle to which only the chloracetic acid was added, but much more slowly in that containing also the neutral salt.

Remark.—The same principle is further illustrated in connection with the two following experiments.

EXPERIMENT XIV.

Principle Illustrated.—The extent to which a weak acid is displaced from one of its neutral salts by another acid added to its solution increases with the degree of dissociation of the added acid. For the displacement depends on the fact that the negative ions of the salt and the hydrogen ions of the added acid when brought together unite in part to form undissociated acid, and the quantity of this which forms is, according to the mass action law, greater, the greater the concentration of the hydrogen ions and therefore the greater the dissociation of the added acid.

Preparation.—Dissolve 6 grams of commercial crystallized alloxan and 2 grams of hydroxylamine hydrochlorate in 200 cc. of water, heat for an hour on a water-bath, and exactly neutralize the solution of violuric acid so prepared with dilute potassium hydroxide solution, with the help of litmus paper, rinsing off the pieces of paper with water after their immersion in the solution, so as to make the color of the litmus evident. (About

55 cc. of a normal solution are required.) Dilute with enough water to make the volume 450 cc. Measure six 50 cc. portions of this solution into six lecture test-tubes 3 cm. in diameter, placed in a rack provided with a background of white paper. Determine accurately the amount of half-normal hydrochloric acid which suffices to decolorize one of these portions to such an extent that it appears of a pale, but distinctly recognizable, pink shade. (Roughly 6 cc. will be required. The exact quantity required is designated M cc. below.) Then entirely decolorize this portion by adding a few more drops of acid. Provide a 10 cc. graduated pipette, an additional lecture test-tube, the four half-normal acid solutions used in Expt. VII, a normal potassium hydroxide solution, a phenolphthalein solution, and a 10 cc. graduate containing a chloracetate solution made by nearly but not quite neutralizing M cc. of the half-normal chloracetic acid with normal potassium hydroxide and diluting up to 10 cc.

Experiment.—Add potassium hydroxide solution in excess to the colorless violuric acid solution, and remove the tube from the rack. Add by means of the 10 cc. graduated pipette to one of the tubes of sodium violurate M cc. of water to serve as a standard and to the four other tubes M cc. of the four half-normal acids in the order acetic, chloracetic, sulphuric, and hydrochloric. Pour one-half of the portion to which the chloracetic acid has been added into the empty test-tube; and add to this 10 cc. of water; and to the half in the original tube add the 10 cc. of chloracetate solution previously prepared after adding to the latter a drop of phenolphthalein solution (to show that it is not alkaline).

Observations.—The colorless violuric acid solution becomes a deep violet when the potassium hydroxide is added. The acetic acid reduces the color to about one-half, and the chloracetic acid to about one-tenth that of the standard; the sulphuric acid gives rise to a pale pink, which, however, is considerably deeper than that produced by the hydrochloric acid. The color of the portion to which both the chloracetic acid and the chloracetate are added is about twice as intense as that of the portion which contains only the chloracetic acid.

Remarks.—The purpose of the addition of potassium hy-

dioxide at the start is to illustrate the facts on which the demonstration of the main principle depends, namely that violuric acid in solution is nearly colorless and that its salt is of a deep violet color. The last part of the experiment on the effect of the neutral salt is a further illustration of the principle here under consideration as well as of that underlying Expt. XIII.

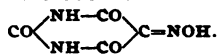
Violuric acid¹ is an acid of about the same strength as acetic acid, the dissociation constants of the two acids being 0.0027² and 0.0018, respectively; consequently, the base divides itself nearly equally between the two acids when, as in the experiment, equivalent quantities of them are simultaneously present. Violuric acid is so very much weaker than sulphuric and hydrochloric acids that it is almost completely displaced by both of them; and, to make evident a difference in their behavior, it is necessary to avoid adding enough hydrochloric acid to cause complete decolorization, and to measure quite accurately the amounts of the two acids added; for 10 per cent. excess of the sulphuric acid entirely obscures the difference in their behavior.

EXPERIMENT XV.

Principle Illustrated.—The behavior of indicators used in titrating acids and alkalies is primarily determined by the principles governing the displacement of one acid (or base) from its salt by another. It depends on the relative degree of dissociation of the indicator, which must itself be a very slightly dissociated acid or base, and of the titrated acid (or base.) The behavior of indicators is in some cases also greatly influenced by the phenomenon of hydrolysis. The behavior of di- and tri-basic acids is dependent on the different degrees of dissociation of the acid with respect to its first and second, or first, second, and third hydrogen atoms. More specific explanations follow the experiments described below.

Preparation.—Place 250 cc. of distilled water in each of ten lecture jars of 400 cc. capacity. Provide the following apparatus and solutions: four 50 cc. graduates; several stirring rods with one end flattened at right angles to the rod; two pipettes with rubber

¹ The constitutional formula of the acid is



² Magnanini: *Ztschr. phys. Chem.*, 12, 58.

nipples for dropping; half-normal solutions of hydrochloric acid and acetic acid, and normal solutions of potassium hydroxide, ammonium hydroxide, sodium acetate, sodium carbonate, and phosphoric acid (made by diluting 12 cc. of sirupy phosphoric acid of 1.34 specific gravity up to 500 cc.); and solutions of phenolphthalein and methyl orange as ordinarily prepared for volumetric analysis.

Experiment.—1. Add from the dropping pipette, to each of four of the lecture jars containing water 3 drops of the normal potassium hydroxide solution. To the first and third of these jars add five drops of phenolphthalein and to the second and fourth add five drops of methyl orange. Then add from the pipette, drop by drop, half-normal hydrochloric acid to the first and second jars, and half-normal acetic acid to the third and fourth jars with constant stirring, until the indicator becomes decolorized or changes color. In the case of the fourth jar, after showing that the first few drops cause no change in color, add the acetic acid in larger quantities from a graduate until about 40 cc. have been added. Then add 25 cc. of normal sodium acetate to both the third and fourth jars.

2. To the fifth jar add just 50 cc. of half-normal hydrochloric acid and five drops of methyl orange. To the sixth jar add the same amount of the hydrochloric acid and two drops of phenolphthalein. Add to each jar from a 50 cc. graduate normal ammonium hydroxide, rapidly until 23–24 cc. are added, and then more slowly until the (sharp) end-point is reached in the fifth jar when about 25 cc. have been added, and until the solution becomes of a decided red color in the sixth jar, requiring about 40 cc. Then add ten drops more of phenolphthalein to the latter.

3. Add to the seventh and eighth jars 25 cc. of normal sodium carbonate, and to the former, five drops of methyl orange, and to the latter, five drops of phenolphthalein. Titrate roughly to an end-point with normal hydrochloric acid, adding from a graduate about 50 cc. to the seventh jar and 25 cc. to the eighth.

4. Add to the ninth and tenth jars 50 cc. of normal phosphoric acid and to the former jar five drops of methyl orange and to the latter five drops of phenolphthalein. Titrate roughly to an end-

point with normal potassium hydroxide, adding from a graduate about 17 cc. to the ninth jar and about 34 cc. to the tenth.

Observations and Explanations.—1. The end-point is sharp and requires for its attainment the same quantity of acid whether hydrochloric acid with phenolphthalein, hydrochloric acid with methyl orange, or acetic acid with phenolphthalein, is used; but when acetic acid and methyl orange are employed, the change of color is very gradual and requires a much larger quantity of acid. These results are explained as follows: hydrochloric acid is so much stronger (*i. e.*, more dissociated) than either phenolphthalein or methyl orange, and acetic acid is so much stronger than phenolphthalein, that the indicator is completely displaced from its potassium salt by even an inappreciable excess of the acid; on the other hand, since methyl orange is a relatively strong indicator-acid¹ and acetic acid a relatively weak acid, a large excess of the latter, whereby a considerable concentration of the hydrogen ions results, is necessary in order to displace the indicator completely from its salt. The sodium acetate added at the close of this experiment causes the yellow color of the methyl orange salt to reappear, owing to the great reduction of the dissociation of the acetic acid, whereby it loses its power of displacing the indicator from its salt; this reduction by the sodium acetate is, however, not sufficient to cause any apparent change in the phenolphthalein equilibrium.

2. In titrating hydrochloric acid with ammonium hydroxide, the end-point is sharp when methyl orange is used, while the change to a pink color is very gradual when phenolphthalein is employed. The remarkable behavior of this last indicator is due to the fact that it is such a very weak acid that when the base also is weak, as is the case with ammonium hydroxide, the salt resulting from their union is so readily decomposed by water that an appreciable quantity of it does not form until the ammonium hydroxide is present in considerable excess; on the other hand, methyl orange is so strong an acid that its salts even with weak bases like ammonium hydroxide are not much hydrolyzed. The addition of more phenolphthalein at the end of the exper-

¹ Other hypotheses in regard to the behavior of this indicator have been proposed by Küster (*Ztschr. anorg. Chem.*, 13, 136) and Waddell (*J. Phys. Chem.*, 2, 171); but these lack experimental verification.

iment intensifies the red color; for it causes, just as the excess of ammonium hydroxide does, a decrease in the amount of hydrolysis.

3. The results observed in this experiment are indicated in the description of it. They are explained as follows: the acid ion HCO_3 , which begins to form on the first addition of hydrochloric acid, is less dissociated than either of the two indicator acids and consequently does not displace either of them from its salts. When a little more than one equivalent of acid has been added, however, the acid H_2CO_3 begins to form, and since its dissociation is greater than that of phenolphthalein but less than that of methyl orange, it displaces the former, giving an end-point, but does not displace the latter.

4. The results are indicated above. They are readily explained with the help of the following assumptions: The acid H_3PO_4 is a stronger acid than either of the indicators; the ion H_2PO_4 is a stronger acid than phenolphthalein, but a weaker one than methyl orange; and the ion HPO_4 is a weaker acid than either of the two indicators.

EXPERIMENT XVI.

Principle Illustrated.—The product of the concentrations of the ions of a salt with which a solution is saturated (the so-called solubility-product) has the same value whether or not other substances are simultaneously present. The presence of a second salt with a common ion therefore reduces the solubility in accordance with this principle; and two different salts, one having in common the positive ion and the other the negative ion of the salt saturating the solution, must have the same effect in reducing the solubility, assuming, as is usually approximately true, that the two salts are equally dissociated.

Preparation of the Experiment.—Prepare 500 cc. of a saturated solution of silver acetate by shaking an excess of the solid salt with warm water, cooling, and filtering or decanting. Place 200 cc. of this solution in each of two 400 cc. lecture jars. Place in graduates 5 cc. of fourfold normal solutions of sodium acetate and of silver nitrate; also provide a stirring rod.

Experiment.—Add the measured portion of sodium acetate to

one jar and that of silver nitrate to the other jar of the silver acetate solution, and stir vigorously for a few moments.

Observations.—A feathery crystalline precipitate of the same character and amount is produced in each jar.

EXPERIMENT XVII.

Principle Illustrated.—The solubility of a salt in water is increased by the addition of a second salt with different ions when there can be produced by metathesis an undissociated substance; and the increase is greater, the greater the amount of this substance formed. Thus, if to saturated solutions of a salt of a partially dissociated acid are added other acids of varying degrees of dissociation, the increase of solubility caused by these will be greater, the greater the degree of their dissociation; for the amount of undissociated acid produced by the metathesis will increase with the increase in the concentration of the hydrogen ions. The formation of the undissociated substance increases the solubility by decreasing the concentration of one of the two ions of the salt saturating the solution, thus making it necessary for more of the salt to dissolve in order to reproduce the original value of the solubility-product.

Preparation.—Treat 10 grams of salicylic acid with a solution of 3 grams of anhydrous sodium carbonate in 100 cc. of water; filter; boil to expel carbon dioxide; add a solution of 9 grams of silver nitrate in 100 cc. of water; and wash and dry the precipitate. Place about 1 gram of it and 45 cc. of water in each of four 50 cc. wide-mouthed, glass-stoppered bottles. Place in each of four lecture jars 10 cc. of hydrochloric acid of 1.12 sp. gr. and 250 cc. of distilled water. Place on the lecture table also the half-normal solutions of sulphuric, chloroacetic, and acetic acids used in Expt. VII; a 5 cc. graduated pipette; a stirring rod; four 25 or 50 cc. graduates with a funnel containing a ribbed filter resting in the top of each.

Experiment.—Add, with the help of the graduated pipette, 5 cc. of the three half-normal acids to three of the bottles containing the silver salicylate. Shake all four bottles vigorously for half a minute and pour their contents on to the four ribbed filters. Allow 25 cc. to collect in each graduate and pour the four

25 cc. portions into the four jars of dilute hydrochloric acid in the order, water, acetic acid, chloracetic acid, and sulphuric acid.

Observations.—The jars to which the water solution and the acetic acid solution are added show a very slight and nearly equal turbidity. The turbidity is much greater in the case of the chloracetic acid, and again much greater in the case of the sulphuric acid.

ON THE PREPARATION OF TRIPHENYLCHLORMETHANE.

BY M. GOMBERG.

Received October 4, 1900.

IT is generally stated in smaller as well as in larger¹ text-books on organic chemistry, that when carbon tetrachloride is treated with benzene and aluminum chloride triphenylchloromethane is the principal product of the reaction. This statement is entirely erroneous.

Friedel and Crafts, who were the first to study this reaction, reported² that they obtained in this way tetraphenylmethane. E. and O. Fischer³ were unable to verify this result, but could obtain only triphenylmethane. It is to be presumed that they carried on this reaction in a manner analogous to that followed in the preparation of triphenylmethane from chloroform, *i. e.*, the resulting products, after being freed from the chloride of aluminum and the excess of benzene, were subjected to fractional distillation at the high temperature of 200°–360° C. Later, Friedel and Crafts⁴ found that the results vary according to the manner of procedure. On distilling the crude products at a high temperature they also obtained triphenylmethane and thus confirmed E. and O. Fischer's results. But if the entire mixture as obtained by the action of aluminum chloride and benzene upon carbon tetrachloride is at once treated with water, it furnishes large quantities of triphenylcarbinol. From this they concluded that the reaction results principally in the formation of triphenylchloromethane, $(C_6H_5)_3C.Cl$, and this on treatment with water furnishes the corresponding carbinol. They confirmed this

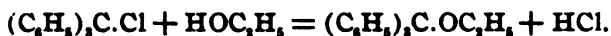
¹ Bellstein: *Handbuch*, II, 287 (3rd edition).

² *Compt. rend.*, 1453 (1877).

³ *Ann. Chem.* (Liebig), 194, 254.

⁴ *Ann. chim. phys.*, I, 497 (1884).

conclusion by the conversion of the crude chloride into the ethoxy compound :



Triphenylmethane is therefore not the first product of the action of benzene upon carbon tetrachloride, but is one of the decomposition products of triphenylchlormethane, formed when the latter is subjected to high heat. That this is likely to occur had been previously shown by E. and O. Fischer on the pure chloro-compound.¹

Of others who have employed Friedel and Crafts' reaction upon carbon tetrachloride itself or upon its phenylated derivatives may be mentioned Doebner and Magati,² Schwartz,³ Weisse,⁴ and V. Meyer.⁵ They all report the formation of triphenylmethane,—due, no doubt, in every instance to the subsequent decomposition of the triphenylchlormethane. In this connection, Nencki and Meissel's work may be mentioned. Nencki⁶ has shown that ferric chloride may with advantage be substituted for aluminum chloride in many syntheses where Friedel and Crafts' reaction is used. According to Meissel,⁷ by the use of this reagent upon a mixture of benzene and carbon tetrachloride, triphenylchlormethane is formed, as by subsequent treatment 75 per cent. of the theoretical amount of triphenylcarbinol can be obtained. "No triphenylmethane is formed in this reaction as is the case when aluminum chloride is employed."

As a matter of fact, however, the action of aluminum chloride upon a mixture of carbon tetrachloride and benzene is exceedingly smooth, provided certain conditions are observed. I have used this reaction many times, and not in a single instance could I detect any trace of triphenylmethane. Friedel and Crafts are entirely correct that triphenylchlormethane is the principal product of the reaction. By observing certain precautions as to temperature of heating and manner of decomposing the chloride of aluminum, the triphenylchlormethane itself can be easily isolated and obtained very pure, with a yield from 70–90 per cent. of the

¹ *Ann. Chem. (Liebig)*, 194, 257.

² *Ibid.*, 12, 1468.

³ *Ibid.*, 14, 1523.

⁴ *Ibid.*, 28, 1537; 29, 1402.

⁵ *Ibid.*, 28, 2792.

⁶ *Ibid.*, 30, 1776; 32, 2415.

⁷ *Ibid.*, 32, 2422.

theoretical quantity. This forms by far the best method for the preparation of this compound, as by means of it one can easily obtain 500 grams of the pure triphenylchlormethane in less than two days. The chloro compound may, therefore, with advantage replace the triphenylbrommethane in many reactions, as the latter is usually made from the rather expensive triphenylmethane. Even by the method of Allen and Kölliker¹ it cannot always be obtained free from the bromanthracenes.

EXPERIMENTAL PART.

Aluminum Chloride.—Gattermann² called attention to the fact that the yield and smoothness of Friedel and Crafts' reaction depend in a great measure upon the purity of the aluminum chloride. He prepared the latter by the action of hydrochloric acid gas upon heated aluminum. This is at present the method generally employed. Biltz³ has noticed that in some instances pure, freshly prepared aluminum chloride is rather a detriment, and old, slightly deteriorated reagent is to be preferred. That chlorine acts upon metallic aluminum is a fact well known, but has seldom been employed in laboratories for the preparation of the chloride.⁴ I find this to be by far the most convenient method of preparing aluminum chloride, especially when one has access to liquid chlorine. The reagent obtained in this manner is very reactive. About 50 grams of aluminum turnings, thoroughly washed and dried, are placed in a combustion tube, the metal being held in place by loose plugs of asbestos wool. The tube is placed in a combustion furnace, one end is connected with the chlorine tank, and the other fits by means of an asbestos stopper into an iron receiver.⁵ The portion of the tube nearest to the receiver is now heated, and a *rapid stream* of dry chlorine is passed into the tube. The gas attacks at once the cold portion of the metal, provided the stream of chlorine is quite rapid. The heat of the reaction is very great, and the metal is kept glowing throughout the length of about 3 inches. In about one and one-fourth to one and one-half hours the reac-

¹ *Ann. Chem.* (Liebig), **227**, 110.

² Stockhausen u. Gattermann: *Ber. d. chem. Ges.*, **25**, 3521.

³ *Ibid.*, **26**, 1960.

⁴ My attention is called to the fact that Erdmann recommends this reaction in his "Introduction to Organic Preparations," p. 43.

⁵ Gattermann: "Praxis des organischen Chemikers," III. Auflage.

tion is finished. The yield is usually 190–200 grams of aluminum chloride, which represents about 80 per cent. of the theory. Sometimes even 90 per cent. can be obtained. By this method 700–800 grams of the chloride can be prepared in one day by using only one furnace. The reagent prepared in this way is very reactive, and retains this property apparently unimpaired even after being kept for two months.

Triphenylchlormethane, $(C_6H_5)_3CCl$.—The proportions which were found to give good results are 1 part of carbon tetrachloride, 3.5 parts of benzene, and about 1.25 parts of aluminum chloride. The carbon tetrachloride and benzene were thoroughly dried over calcium chloride and carefully fractionated. The two liquids are placed in a round-bottomed flask connected with a long inverted condenser by an arrangement as suggested by Anschütz.¹ The aluminum chloride is added in portions of about 20 grams each. The reaction becomes very violent. I have not attempted to moderate it by cooling. After all the chloride is added, the mixture is heated on the water-bath for about an hour. The next step, the decomposition of the aluminum chloride, requires certain precautions. The cooled mixture is poured in a slow stream upon a good quantity of pounded ice, the jar containing the latter being itself surrounded with a cooling mixture. The addition of the reaction product to the ice should be done slowly, and with constant stirring. Benzene is also added from time to time in order to keep the triphenylchlormethane in solution. After all has been added the benzene solution is separated from the ice and water by a separating funnel, shaken once with ice-water containing hydrochloric acid, and once with ice-water alone. It is advisable to leave the two solutions in contact with each other as short a time as possible. The filtered benzene solution is dried thoroughly over calcium chloride, and concentrated on the water-bath as far as possible. On cooling, over half of the pure triphenylchlormethane separates in large crystals. These are removed by filtration and washed once or twice with dry ether, in which the chloro compound is not very soluble. The filtrate is distilled first on a water-bath at ordinary pressure, and then concentrated by distilling off the benzene under diminished pressure. To the very concentrated solution dry ether is again

¹ *Ann. Chem.* (Liebig). 235, 154.

added, and another large portion of the chloro compound is precipitated. This is treated in the same way as the first crop of crystals, and is just as pure, retaining a slight pink color. The mother liquid is subjected once more to the same treatment—evaporating the ether, and concentrating under diminished pressure—and yields a third crop of crystals. By this treatment the triphenylchlormethane is freed from both the coloring-matter and the triphenylcarbinol, since both of these are quite soluble in ether. The last mother-liquid contains all the coloring-matter. In several instances I have evaporated it to a thick sirup, dried on a porous plate, boiled with water, and obtained considerable quantities of triphenylcarbinol,—but never any indication of triphenylmethane. The yield of the pure chloro compound varies from 70–85 per cent. and enough carbinol can be obtained to account for a yield of 90–95 per cent. of the theory.

In the following table are given some of the results obtained:

	Carbon tetra- chloride. Grams.	Benzene. Grams.	Aluminum chloride. Grams.	Triphenyl- chlor- methane. Grams.	Per cent. of theory.	Triphenyl- carbinol. Grams.
I	300	1000	300	390	72	22
II	360	1500	410	500	71	..
III	39	150	50	51	78	10
IV	129	500	150	201	87	..

It has already been mentioned that the triphenylchlormethane obtained by this reaction is quite pure, and can be employed for most reactions without further purification. It melts usually at 108° – 112° C., while Hemilian¹ gives it as 105° – 115° C.

The following method was found to give equally good results as Carius' for the estimation of chlorine in this substance. The chloro compound is dissolved in alcoholic potash (2 per cent.) and heated for a short time on the water-bath. The alcohol is evaporated, the residue dissolved in water, filtered from the ethyl ether of triphenylcarbinol, and the chlorine is estimated in the filtrate in the usual manner with silver nitrate.

In the following table are given the results of analysis of I, III, IV of the preceding table. The chloro compound had been obtained in three separate crops. Each crop was analyzed by itself.

¹ *Ber. d. chem. Ges.*, 7, 1203.

	First crop.	Second crop.	Third crop.	Calculated for (C ₆ H ₅) ₃ C.Cl.
I.....	12.35	12.74	12.69	12.75
III.....	12.45	12.48	12.49	12.75
IV.....	12.62	12.60	12.56	12.75

The product obtained by this method may, therefore, be considered quite pure. For further purification it can be recrystallized from benzene alone, or better by precipitating it from a concentrated solution in benzene by means of dry ether. By this method large quantities of pure triphenylchlormethane can be more easily obtained than by the old method¹,—by treating triphenylcarbinol with phosphorus pentachloride.

In conclusion I wish to express my thanks to Messrs. A. G. Marion, H. W. Emerson, and F. L. Woods for their kind assistance in carrying out some of the experimental work.

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AN INSTANCE OF TRIVALENT CARBON: TRIPHENYL-METHYL.

BY M. GOMBERG.

Received October 4, 1900.

[PRELIMINARY PAPER.]

SOME time ago¹ I published a method of preparing tetraphenylmethane. The yield was rather small and I was obliged to study the solubilities, composition, molecular weight, and the nitro derivative on about 0.5 gram of the hydrocarbon. The stereochemical interest attached to this compound has induced me to take up the subject once more, in the hope of obtaining larger yields. I have, therefore, gone over most of the methods which have been tried by others for the preparation of tetraphenylmethane. My results, while differing in detail from those published by others, agree in the main,—the hydrocarbon could not be obtained by the usual reactions. One of the main proofs advanced by me for the constitution of tetraphenylmethane was that it furnished a tetranitro derivative which gave no colored salts with alcoholic potash, while most of the less phenylated methanes do respond to this test. To prove whether

¹ Hemilian: *Ber. d. chem. Ges.*, 7, 1207.

² *Ber. d. chem. Ges.*, 30, 2043; *This Journal*, 20, 773.

this reaction could safely be relied upon I decided to prepare hexaphenylethane, $(C_6H_5)_3C-C(C_6H_5)_3$. This hydrocarbon should by nitration give a hexanitro body with no hydrogen attached to the ethane carbon atoms. Consequently it also should give no colored salts with sodium ethylate or alcoholic potash.

Accordingly, triphenylbrommethane in benzene was treated with metallic sodium, but without success. The chloro compound gave no better results. Molecular silver was substituted for sodium. After several hours' boiling a white crystalline body began to separate, and on filtering the hot benzene solution a considerable amount of the same substance separated on cooling. It was recrystallized from benzene, gave a constant melting-point, $185^\circ C.$, and contained no halogen. In its high melting-point and in its only slight solubility in the usual organic solvents it resembled closely tetraphenylmethane, and this new body was taken for hexaphenylethane. An elementary analysis gave, however, the following results :

	Calculated for $(C_6H_5)_6C_2$	Found.
Carbon	93.83	87.93
Hydrogen	6.17	6.04

The low per cent. of carbon found was rather surprising. It was explained on the assumption that this was, perhaps, an instance of a hydrocarbon which is not easily burnt. The next combustion was, therefore, carried on in an atmosphere of oxygen from the very beginning. The substance was mixed in the tube with copper oxide; a very high heat was applied towards the end of the combustion. The results were as follows :

Carbon	87.74
Hydrogen	6.46

An entirely new lot of the material was then prepared. Ten grams of triphenylchlormethane and 10 grams of silver gave, after several hours' boiling, 4 grams of the same hydrocarbon. This was recrystallized twice from benzene and twice from chloroform. It was perfectly free from halogen, was snow-white, and melted at $185^\circ-186^\circ C.$ The combustion was again made in an atmosphere of oxygen, lead chromate being used instead of copper oxide.

Carbon	87.77
Hydrogen	6.23

The next analysis was made in a bayonet tube, the tube being filled with fine copper oxide for about four-fifths of its length, to insure combustion of any methane gas which would perhaps otherwise escape. The combustion was carried on slowly, and a very high heat was used towards the end.

Carbon	88.23
Hydrogen	6.34

Several new lots of the same substance were made both from the triphenylbrommethane and triphenylchloromethane, and purified by successive recrystallization from benzene, chloroform, acetic ether, and carbon disulphide. They all gave the same results, entirely concordant with each other. Combustions were then made in a porcelain tube, applying the direct heat of the furnace; also by the moist method with chromic acid in concentrated sulphuric acid,¹ but with no better result. I therefore came to the conclusion that the body under consideration was not a simple hydrocarbon, but an oxygen derivative. The oxygen could come from either of two sources: first, the molecular silver may have contained some oxide of the metal; second, the atmospheric oxygen may act upon the hydrocarbon.

As only the molecular silver, and not the finely powdered crystalline metal appeared to act in this case, a very pure sample of the former was prepared. The moist silver, as obtained by reduction of the chloride with zinc, was digested for a day with dilute sulphuric acid. It was then thoroughly washed by decantation, digested for several hours with ammonium hydroxide, again washed with water, then with alcohol, absolute alcohol, ether, and finally with benzene. This sample of silver gave, however, results not differing from those previously obtained. To make it more certain that the oxygen did not come from the silver, I substituted other metals for it. Mercury and zinc were found to act equally well, if not better, and the yield of the oxygen compound obtained by either of these two metals was even greater than in the case of silver. Another great advantage in the use of zinc and mercury is that the reaction takes place at *ordinary temperature*. Mercury is especially well suited for a

¹ Fritzsche: *Ann. Chem.* (Liebig), 294, 79.

lecture experiment showing this reaction. If a benzene solution of triphenylchlormethane or triphenylbrommethane beshaken in a test-tube for a few minutes with some metallic mercury and the solution rapidly filtered, the separation of the insoluble oxygen compound in the filtrate will soon begin, due to the absorption of atmospheric oxygen.

I next proved that it is really the oxygen from the atmosphere which oxidizes the hydrocarbon. By working in an atmosphere of carbon dioxide no such insoluble compound is produced, even on weeks' and months' treatment of the halogen bodies with silver, mercury, or zinc in benzene. After a long series of experiments I settled upon zinc as the best reagent with which to carry on this reaction. Ordinary granulated zinc, zinc strips, zinc dust,—all act upon the halogen compounds. In all further experiments what is known as *powdered zinc*, freed from zinc dust by sifting, has been employed. In this form the metal can readily be obtained free from the oxide, is easily handled, has a large surface exposure, and presents no difficulties in filtering from the benzene solution. Triphenylchlormethane¹ has been used altogether instead of the bromine compound.

The successful preparation of the unsaturated hydrocarbon requires the *absolute* exclusion of oxygen from the apparatus. Corks are to be avoided, and even rubber stoppers, exposed to the action of benzene vapors, become after a while porous. I have constructed for this work an apparatus by means of which the reaction can be carried on for several weeks, and months, if necessary. The zinc, benzene, and triphenylchlormethane are first digested for any length of time desired at ordinary temperature; the solution is then filtered into a distilling flask and the zinc washed with fresh portions of benzene. The combined liquids are distilled under diminished pressure at 30° C., and the solid crystalline residue containing the unsaturated hydrocarbon can be examined as to its solubility in different solvents, or treated in any manner desired. The apparatus is so arranged that all these steps are carried on in an atmosphere of dry carbon dioxide. Only ground-glass joints are used. The description of the apparatus is reserved for a future paper.

¹ For the preparation of this see the preceding paper.

I THE HALOGEN IS TAKEN OUT BY THE ZINC QUANTITATIVELY.

The zinc removes the halogen from triphenylchlormethane quantitatively at ordinary temperature. The zinc chloride separates as a thick dark yellow sirup, probably forming a compound with benzene similar to the one produced by aluminum chloride. This is of very great advantage, because by this means fresh, clean surfaces of the metal are continually exposed for further action. For this reason the reaction is very slow, and soon stops altogether when carbon tetrachloride is substituted for benzene. With 20 grams of triphenylchlormethane, 150 grams of benzene, and 25 grams of zinc the reaction is completed in about five to six days. After removing the benzene solution and washing the residue thoroughly with benzene, the zinc chloride was dissolved in water and the chlorine estimated in the usual way.

	Triphenyl- chlormethane taken. Grams.	Number of days of digestion.	Chlorine as ZnCl ₂ .	Calculated.
I	5	12	12.61	12.75
II	20	5	12.25	12.75
III	20	20	12.41	12.75

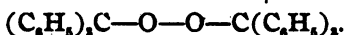
II. THE UNSATURATED HYDROCARBON.

The clear filtered solution containing the unsaturated hydrocarbon is concentrated under diminished pressure at a temperature of 30°–35° C., a slow stream of carbon dioxide being used to prevent bumping. When all the benzene has been distilled off, a strong stream of the gas is allowed to bubble through the thick yellow sirup, while the temperature is raised to about 40° C. On cooling, the whole residue solidifies to a crystalline cake, which does not melt even at 60° C. Even after several weeks' standing it redissolves readily in benzene with the exception of some of the oxygen compound whose formation is due to unavoidable leakage of the stop-cocks. The hydrocarbon is quite soluble in chloroform, less so in carbon tetrachloride, and is quite readily dissolved by carbon disulphide. If a concentrated solution of it is allowed to stand for three or four weeks, some large transparent crystals are formed. An attempt was made to remove these and wash with petroleum ether, but before the operation was finished enough oxygen was absorbed to form the

insoluble derivative. I hope to be able to isolate the hydrocarbon itself in a pure state.

The body is extremely unsaturated. A solution of it in benzene or in carbon disulphide absorbs oxygen with great avidity and gives an insoluble oxygen compound. It absorbs chlorine, bromine, and iodine. It does not unite with carbon monoxide.¹

III. DI-TRIPHENYLMETHYLPEROXIDE,



The crystalline compound which is formed by the action of the atmospheric oxygen upon a solution of the unsaturated hydrocarbon, is the peroxide of triphenylmethyl. It is best prepared by passing air or oxygen through a solution of the hydrocarbon in benzene. Twenty grams of the halogen compound give about 12 grams of the peroxide. The elementary composition fully agrees with that required by the formula :

	Calculated for (C_6H_5) ₆ C_2O_2 .	I.	II.	Found. III.	IV.	V.
Carbon.....	88.03	87.93	87.74	87.77	88.22	87.60
Hydrogen.....	5.79	6.04	6.46	6.23	6.34	6.09

This body is characterized by extreme insolubility. It is only with difficulty dissolved by hot benzene, toluene, and then not without some decomposition. It can be recrystallized from chloroform. It is insoluble in ether, alcohol, and water. It is best recrystallized from carbon disulphide, 1 gram dissolving in about 150 cc. of the hot solvent. I have obtained by the use of this solvent remarkably beautiful and regular crystals, six-sided hexagons, of a very high refractive index. The peroxide melts at 185°-186° C. (uncorr.)

It is quite stable on exposure to air but decomposes gradually when a solution of it is heated. For this reason solvents of low boiling-point are to be preferred.

Formation by Means of Sodium Peroxide.—On heating triphenylchloromethane in benzene with commercial barium peroxide for several days a small amount of the triphenylperoxide was obtained. On repeating the experiment with a purified sample of barium peroxide the result could not be duplicated. I have resorted to the use of sodium peroxide, and with this

¹ Compare Nef: *Ann. Chem.* (Liebig), 270, 267.

reagent I never failed to get the peroxide. A 10 per cent. solution of sodium peroxide is made by dissolving the latter in ice-water. Three to four grams of triphenylchlormethane in just enough benzene to make a clear solution are added, and a stream of air, free from carbon dioxide, is passed through the cold mixture until all the benzene is evaporated. The air keeps the two liquids in constant motion and fresh quantities are continually exposed to action. The solution is now filtered and washed. The unchanged chloro compound and the carbinol are removed by ether and the insoluble residue is boiled up with a large amount of carbon disulphide. The filtered solution gives, on concentration, a small amount of the characteristic crystals of the peroxide. This method was repeated several times, with and without the use of benzene, and has invariably given from 5 to 10 per cent. of the calculated amount of the peroxide. The larger portion of the chloride is changed to the carbinol, as it always does when left in contact with water, especially in presence of alkalies. The peroxide so obtained was identical with the one previously described. An analysis gave the following figures :

	Calculated for (C ₆ H ₅) ₃ C ₂ O ₂ .	Found.
Carbon	88.03	87.55
Hydrogen	5.79	6.00

That the formation of the peroxide is really due to the presence of sodium peroxide, and does not result from the oxidation of the chloride or the carbinol by atmospheric oxygen, is shown by the following experiment : Three grams of the chloride dissolved in 10 cc. of benzene, were added to 100 cc. of a 10 per cent. solution of sodium hydroxide, and air was passed through the flask exactly in the same way as when sodium peroxide was used. On working up the product not a trace of triphenylmethylperoxide was found.

Molecular Weight.—Attempts to get an exact determination of the molecular weight have not proved as successful as desired. The peroxide is only slightly soluble in the usual organic solvents, and, therefore, only a slight elevation of the boiling-point could be expected, from 0.003°-0.150° C. I have found no liquid or low-melting solvent which could be used for the freezing-point

method. In using the boiling-point method it was found necessary to select as low-boiling a solvent as possible, since the peroxide suffers gradual decomposition at higher temperatures. Carbon disulphide was tried first. As the solubility of the peroxide in this solvent is only about 1 gram in 150 cc., the maximum rise of temperature could not be expected to be above 0.040° C. I therefore constructed an apparatus similar to the one described by Jones.¹ From 100–200 grams of the solvent could then be employed for a single determination. By this means the influence of the absolute error due to the weighings, vaporization of the solvent, etc., is greatly reduced. The apparatus proved very reliable, and the solvents employed could be kept boiling for an hour with a variation of temperature not exceeding 0.002° C. Tested on triphenylmethane the apparatus gave a molecular weight of 252 (244 calculated) when 1.2862 grams of the substance and 113 grams of the solvent were employed. The rise of temperature was to 0.107° C.

SOLVENT : CARBON DISULPHIDE. $K = 2370$.

Carbon Disulphide. Grams.	Peroxide. Gram.	Rise in boiling-point.	Calculated rise for $m = 518$.	Molecular weight.
121.7	0.7300	0.035	0.028	406

The temperature remained constant for about fifteen to twenty minutes; after that it gradually began to rise, about 0.001 every ten minutes. The experiment was interrupted when 0.045 was reached. The solution was yellowish, showing slight decomposition of the peroxide.

SOLVENT : BENZENE. $K = 2770$.

Benzene. Grams.	Peroxide. Grams.	Rise in boiling-point.	Calculated rise for $m = 518$.	Molecular weight.
66	0.853	0.09	0.070	448

This temperature remained constant for about ten minutes, after that the rise was gradual until in an hour it reached 0.185° C. The solution was then quite yellow.

Ethylene dibromide was also tried, but as this boils still higher, there was even more rapid decomposition. The results in the main agree with those obtained when benzene was used.

The only conclusion that can be safely drawn from these results is that we have here a substance of very high molecular

¹ *Am. Chem. J.*, 19, 581.

weight, above 400 at least. The formula for the peroxide would require 518.

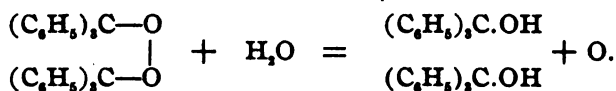
Conversion of the Peroxide into the Carbinol.—The peroxide dissolves in cold concentrated sulphuric acid with considerable evolution of heat, giving a yellow solution which soon turns dark, and finally almost black. The sulphuric acid does not induce any explosion as is the case with most organic peroxides. On diluting the acid with water the triphenylcarbinol is precipitated out as a dark flocculent precipitate.

2.85 grams of the pure peroxide were dissolved in 25 cc. of sulphuric acid and allowed to stand over night. The solution was then poured upon ice and the precipitate separated by filtration. It was dissolved in ether, and the dark ethereal solution was repeatedly shaken with dilute sodium hydroxide until the ether was only of a pale yellow color. The dried ethereal solution was then concentrated to a small bulk and rhigolene added. Crystals of triphenylcarbinol separated and were almost pure, melting at 159° – 160° C. The yield was 1.948 grams, which represents 70 per cent. of the peroxide taken. The mother-liquid, on concentration, gave additional 0.215 gram, and 0.050 gram was obtained from the third crop, making a total of almost 80 per cent. The remaining 20 per cent. were probably oxidized by the oxygen evolved or perhaps sulphonated, as the sodium hydroxide removes all the dark color from the ethereal solution. An analysis gave the following results :

0.2910 gram substance gave 0.9330 gram carbon dioxide and 0.1654 gram water.

	Calculated for (C ₆ H ₅) ₃ C.OH.	Found.
Carbon	87.69	87.44
Hydrogen	6.15	6.31

The reaction may therefore be represented by the following equation :



Di-trinitrotriphenylmethylperoxide, (C₆H₄NO₂)₃C—O—O—C(C₆H₄NO₂)₃.—Brodie,¹ Vanino,² and Nef³ have shown that the

¹ *Ann. Chem. (Liebig)*, Suppl. III, 209.

² *Ber. d. chem. Ges.*, 30, 2004; 33, 1045.

³ *Ann. Chem. (Liebig)*, 298, 287.

superoxides of acid radicals can be nitrated with fuming nitric acid. The peroxide here described shares the same property. It forms very readily a hexanitro compound. One gram of the peroxide gave 1.375 grams of the pure nitro body, while theory requires 1.555 grams. The nitro compound is insoluble in the usual organic solvents. One gram refuses to dissolve completely in 500 cc. of boiling glacial acetic acid. It is best recrystallized by dissolving it in nitrobenzene at 120°–130° C., and precipitating with petroleum ether.

	Calculated for $C_{20}H_{12}N_6O_{14}$	I.	Found. II.
Carbon.....	57.87	57.55
Hydrogen.....	3.05	3.34
Nitrogen.....	10.65	11.03	10.94

IV. TRIPHENYLIODOMETHANE, (C_6H_5)₃C.I.

The unsaturated hydrocarbon, which is formed when the halogen is removed from triphenylchlormethane, unites not only with oxygen, but also instantly with chlorine, bromine, and iodine. The reaction with chlorine and bromine is, however, not one of mere addition. The hydrocarbon is so reactive that even at –10° C. chlorine and bromine act both by addition and substitution. When the hydrocarbon, entirely freed from benzene, is dissolved in carbon tetrachloride there is always some hydrochloric and hydrobromic acid produced on the addition of the halogen. Triphenylchlormethane and triphenylbrommethane are among the products but it is not easy to separate the substitution halogen-compounds formed at the same time. This reaction will be further studied.

Iodine is absorbed by the hydrocarbon as readily as the other two halogens. When a solution of the hydrocarbon in carbon disulphide is treated at 0° C. with a solution of iodine in the same solvent, the latter is instantly decolorized. The end-reaction is quite sharp. In one instance, working with a product from 20 grams of triphenylchlormethane, 6 grams of iodine were absorbed, which is equivalent to 12 grams of (C_6H_5)₃C—; in another case, where 25 grams of the chloro compound were employed, the absorption amounted to 8 grams of iodine. The isolation of the iodo compound requires considerable precautions, as it is a very

unstable body. I have found it best to work in an atmosphere of dry carbon dioxide, but am not as yet prepared to say whether it is the oxygen or the moisture of the air that affects it most. Probably it is the latter. The solution of the iodo compound was filtered to remove a slight amount of a periodide¹ and the peroxide. To the clear carbon disulphide solution rhigolene was added and the mixture cooled in ice. After some crystals had separated the liquid was transferred to another flask and cooled again, when more crystallized out. This last crop was recrystallized by dissolving it in carbon disulphide and precipitating with rhigolene. The crystals were of a pale yellow color, the same in appearance as the chloro compound when the latter is similarly precipitated. The crystals were washed several times with rhigolene and dried rapidly *in vacuo*.

The iodine was estimated by treating a weighed sample of the compound in dilute alcohol with ammonia and zinc dust. The hot alcoholic solution was filtered, the zinc washed thoroughly with hot alcohol, and then with water. The alcohol washings were concentrated, filtered, and the residue was exhausted with water. The insoluble portion was purified with ether, and was identified as triphenylcarbinol. It melted at 153°C ., probably due to the presence of some triphenylmethane. On recrystallizing twice from alcohol the melting-point was raised to 157° – 159°C . The yield of the carbinol was 0.383 gram, while the calculated quantity for the 0.602 gram of triphenyliodomethane was 0.422 gram.

0.602 gram substance gave 0.3704 gram AgI.

	Calculated for (C_6H_5) ₃ C.I.	Found.
Iodine.....	34.29	33.23

The iodide turns dark very readily and loses iodine. It is very unstable. It melts approximately at 135°C ., with decomposition. Water, especially in the presence of alkalis, converts it into triphenylcarbinol, a reaction similar to that with the corresponding chloro and bromo compounds. Alcohol, however, behaves in this case differently. On boiling with alcohol large quantities of iodine are set free and the body is reduced by the

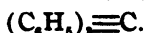
¹ For a periodide of triphenylbrommethane, see this Journal, 20, 790.

alcohol to triphenylmethane, while in the case of triphenylchloromethane and triphenylbrommethane the ethyl ether,

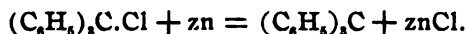


is formed. The triphenylmethane was freed from a small amount of the unreduced ether by fractional crystallization from alcohol, and was identified by its characteristic crystals containing benzene of crystallization and melting at 77°C . On exposure to air the benzene of crystallization was lost and the crystals melted at 92°C .

V. TRIPHENYLMETHYL,



The experimental evidence presented above forces me to the conclusion that we have to deal here with a free radical, triphenylmethyl, $(\text{C}_6\text{H}_5)_3\equiv\text{C}$. On this assumption alone do the results described above become intelligible and receive an adequate explanation. The action of zinc results, as it seems to me, in the mere abstraction of the halogen, leaving the free radical,

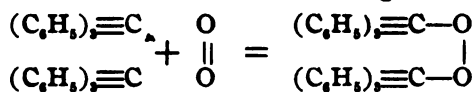


The radical so formed is apparently stable, for it can be kept both in solution and in the dry crystalline state for weeks. The radical refuses to unite with another one of its kind, and thus forms a distinct exception to all similar reactions. It might be said that, perhaps, it does polymerize to hexaphenylethane, $(\text{C}_6\text{H}_5)_3\text{C}-\text{C}(\text{C}_6\text{H}_5)_3$, but this hydrocarbon is so unstable that mere exposure to air is sufficient to break it down. Such an assumption seems to me less tenable than that of a free radical. Hexaphenylethane must, according to all our present notions of valence, be a saturated compound. Yet the hydrocarbon under consideration is decidedly unsaturated. We know of no better positive test for unsaturation in hydrocarbons than the absorption of halogens. Perhaps chlorine and bromine would in this case attack and decompose hexaphenylethane, if that be the hydrocarbon; but, certainly, a dilute solution of iodine, at 0°C ., would scarcely do that. It seems to me rather that hexaphenylethane, once formed, would prove quite a stable compound. This may be justly inferred from analogous reactions, where a

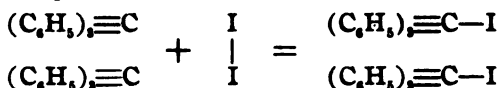
¹ Hemilian: *Ber. d. chem. Ges.*, 7, 1208.

fourth heavy radical has been successfully introduced into the methane,—as is the case with triphenylthiophylmethane, $(C_6H_5)_3C.C_6H_4S$,¹ tetraphenylmethane, $(C_6H_5)_4C$,² triphenylacetic acid,³ etc. It is a phenomenon parallel to that expressed by V. Meyer's esterification law of diortho substituted aromatic acids: It is very difficult to introduce an alkyl into the carboxyl of such acids by the *usual method* of esterification, but once introduced, it is just as difficult to remove it again.

On the assumption of the existence of triphenylmethyl itself, as such, all the reactions of the unsaturated body become clear. Oxygen adds itself, a whole molecule, and gives the peroxide:



The addition of a molecule of oxygen is entirely in accord with the recent studies of M. Traube, van't Hoff, Engler, Manchot, Bach, Baeyer and Villiger, and Nef. This case forms an excellent illustration of Engler's theory that "autoxidation" results first of all in the formation of superoxides. The action of halogens upon the unsaturated body is primarily that of addition. Thus iodine gives triphenyliodomethane:



That the unsaturated hydrocarbon is not the result of some complicated reaction between triphenylchlormethane, benzene, and the nascent zinc chloride formed during the experiment, is proved by the following: 5 grams of the halogen compound were dissolved in 100 cc. of carbon disulphide and shaken at intervals with 100 grams of metallic mercury for two days. The clear filtered solution on exposure to air furnished 3.8 grams of triphenylmethyl peroxide. Five grams of triphenylchlormethane, treated with zinc and benzene for four days, gave 3.1 grams of the peroxide.

The existence of triphenylmethyl implies, of course, the existence of *trivalent carbon*, at least in this particular instance. The

¹ Weiss: *Ber. d. chem. Ges.*, 28, 1538.

² Gomberg: *Ibid.*, 30, 2043.

³ E. and O. Fischer: *Ann. Chem. (Liebig)*, 194, 260; Heyl and V. Meyer: *Ber. d. chem. Ges.*, 28, 2782.

⁴ *Ber. d. chem. Ges.*, 30, 1669; 33, 1090, 1097.

conception of such a trivalent carbon in this instance is entirely distinct from that which is ascribed to it by some in benzene, or even in ethylene, where there are always *two* adjoining carbon atoms acting as trivalent. The unsaturation in such cases has always been indicated by a "double linking." In triphenylmethyl there is *only one carbon atom* that is unsaturated. The existence of such a body means that when three valences of carbon are taken up by three phenyl groups it is difficult, or perhaps even impossible, to introduce as a fourth group such a complicated radical as $(C_6H_5)_3C-$. Only simpler groups, chlorine, bromine, iodine, oxygen, etc., may still combine with such a carbon atom. Whether this be due to the negative character of the three phenyl groups, or whether it is caused by the fact that these groups take up so much space around the carbon atom as to hinder the introduction of another complicated group, is a question of an entirely different nature and need not be discussed here. There are, however, numerous reactions which go to show that there is a limit to the number of complicated groups which can ordinarily be linked to one and the same carbon atom. A few of these reactions may be mentioned.

Hemilian,¹ Friedel and Crafts,² E. and O. Fischer,³ Magati,⁴ Schwartz,⁵ V. Meyer,⁶ Weisse,⁷ Waga,⁸ and Meisel,⁹ have all attempted to prepare tetraphenylmethane, but in all cases triphenylmethane resulted. Even such comparatively simple compounds as $(C_6H_5)_3C.C_2H_5$,¹⁰ or $(C_6H_5)_3C.CH_3$,¹¹ could not be obtained by reactions from which, *a priori*, we should certainly expect the formation of such bodies. The disinclination of carbon to hold more than three complicated groups is well illustrated by the results of Anschütz's¹² extended researches on tetraphenylethane. A large number of methods which ought to give the unsymmetrical derivative, $(C_6H_5)_3C.CH_2(C_6H_5)$, always

¹ *Ber. d. chem. Ges.*, 7, 1209.

² *Ann. chim. phys.*, 1884, I, 497.

³ *Ann. Chem. (Liebig)*, 194, 254.

⁴ *Ber. d. chem. Ges.*, 12, 1468.

⁵ *Ibid.*, 14, 1523.

⁶ *Ibid.*, 28, 2792.

⁷ *Ibid.*, 28, 1538; 29, 1402.

⁸ *Ann. Chem. (Liebig)*, 282, 330.

⁹ *Ber. d. chem. Ges.*, 32, 2422.

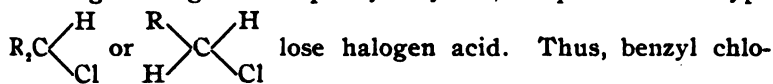
¹⁰ E. and O. Fischer: *Ann. Chem. (Liebig)*, 194, 259.

¹¹ Biltz: *Ibid.*, 296, 253.

¹² *Ibid.*, 238, 203.

give the symmetrical one, $(C_6H_5)_3CH \cdot CH(C_6H_5)_3$. And lastly, the abnormal behavior of tetraphenylethylene towards bromine, as found by Biltz,¹ shows again the same point. Bromine will substitute in, but not add itself to, tetraphenylethylene, although we have here an unsaturated linking, $(C_6H_5)_2C : C(C_6H_5)_2$. These and a number of other facts show conclusively that with three valences of carbon taken up by such complicated or large groups as phenyl, the fourth valence can ordinarily be linked to atoms or groups of simple construction only. Now, as a result of the removal of halogen from triphenylchlormethane in benzene by zinc, or in carbon disulphide by mercury, the fourth valence of the methane carbon is bound either to take up the complicated group $(C_6H_5)_3C-$, and polymerize, or remain as such, with carbon as trivalent. Apparently the latter is what happens.

In conclusion, it may be mentioned that the action of metals upon triphenylhalogenmethane has been tried before. Elbs² acted upon triphenylbrommethane with sodium, magnesium, and copper. Anschütz³ employed sodium upon a mixture of triphenylbrommethane and benzyl chloride. The action of metals upon the di- and monophenylhalogen methanes has also been extensively studied. While diphenyldichlormethane loses all its halogen and gives tetraphenylethylene, compounds of the type



ride, when treated with zinc,⁴ zinc-copper couple,⁵ gives polymers and reduction-products of phenylmethylene. Recently Nef⁶ has used aluminum chloride upon benzyl bromide in the hope of splitting off hydrobromic acid and thus obtaining the free radical phenylmethylene, $(C_6H_5)CH$. The formation of the latter as an intermediate product was made quite probable, but the isolation of it proved impossible, owing to a rapid polymerization.

This work will be continued and I wish to reserve the field for myself.

UNIVERSITY OF MICHIGAN,
CHEMICAL LABORATORY,
August, 1900.

¹ Ann. Chem. (Liebig), 296, 231.

² Ber. d. chem. Ges., 17, 700.

³ Ann. Chem. (Liebig), 235, 226.

⁴ Zincke: *Ibid.*, 159, 1368.

⁵ Gladstone and Tribe: *J. Chem. Soc.*, 45, 154; 47, 448.

⁶ Ann. Chem. (Liebig), 298, 248.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 52.]

THE SEPARATION OF TUNGSTEN TRIOXIDE FROM MOLYBDENUM TRIOXIDE.

BY MAX J. RUEGENBERG AND EDGAR F. SMITH.

Received September 7, 1900.

THE separation of tungsten from molybdenum is always of interest to those who are brought in contact with analytical methods. It has been the subject of numerous investigations and much discussion, and while comparatively good methods exist for this purpose, the analyst continues to seek for others, hoping that eventually he shall find a procedure which will be satisfactory in all respects and under nearly all conditions.

The writers have not discovered the method *par excellence*, but desire to offer briefly, in the following lines, their experience in pursuing a suggestion made in an article emanating from this laboratory; *viz.*, "tungstic acid is insoluble in concentrated or dilute sulphuric acid, hot or cold, whereas molybdenum trioxide is very easily and rapidly dissolved, so that we have in this department a very simple and exact method for the separation of the two metals."¹

No analytical data accompanied this declaration; therefore it seemed not improper to attempt to learn the conditions most favorable for the separation. Upon trial it was found that sulphuric acid of specific gravity 1.378, dissolved molybdenum trioxide very readily and apparently did not affect the tungsten trioxide. Acid of this concentration was, therefore, used with the following mixture of the two oxides:

I. 0.7355 gram of tungsten trioxide and 0.0185 gram of molybdenum trioxide were digested for a few minutes with 25 cc. of warm sulphuric acid. The insoluble portion was filtered out and washed with water containing sulphuric acid. After drying it was ignited and weighed. It equaled 0.7350 gram.

The other trials, conducted in precisely the same manner, were as follows:

	II. Grams.	III. Grams.	IV. Grams.	V. Grams.	VI. Grams.
Tungsten trioxide taken	1.0638	0.0871	0.3588	0.8868	0.5996
Molybdenum trioxide taken	2.2712	0.6871	1.1836	1.1986	1.0770
Tungsten trioxide found ...	1.0630	0.0870	0.3587	0.8866	0.5996

¹ En. D. Deal: This Journal, 19, 242.

The filtrate containing the dissolved molybdic acid showed no tungstic acid upon examination.

These results indicate that where the two oxides are present together this mode of separation is apparently of value and merits consideration.

A weighed quantity of a ferric salt equivalent to 5 grams of ferric hydroxide was precipitated with ammonia water and the resulting precipitate, after being washed, was mixed in a beaker with different amounts of tungsten trioxide, and the resulting mixture was then digested with sulphuric acid of the strength of that used in the preceding experiments. The residual oxide was treated as before :

	I. Grams.	II. Grams.	III. Grams.	IV. Grams.	V. Grams.	VI. Grams.
Tungsten trioxide taken ..	0.5282	0.2087	1.3270	0.2004	0.9091	0.2263
Ferric hydroxide taken ...	5.0000	5.0000	5.0000	5.0000	5.0000	5.0000
Tungsten trioxide found ..	0.5278	0.2086	1.3265	0.2003	0.9088	0.2262

We may conclude from these trials that the solubility of the trioxide in the sulphuric acid is in no wise affected by the presence of the iron.

UNIVERSITY OF PENNSYLVANIA.

NEW BOOKS.

THE MINERAL INDUSTRY: ITS STATISTICS, TECHNOLOGY, AND TRADE IN THE UNITED STATES AND OTHER COUNTRIES, TO THE END OF 1899. EDITED BY RICHARD P. ROTHWELL. Vol. VIII. Large 8vo. xxviii+986 pp. With many illustrations. New York: The Scientific Publishing Co. Price, \$5.00.

This new annual volume of a well-known and greatly valued series fully sustains the reputation already obtained. The difficulty in obtaining accurate information of this character is well known, and the rapid publication of a large volume like this, requiring the cooperation of so many persons, reflects the greatest credit upon all those concerned in it. The year 1899 was a great year for the mineral industry in the United States, the production in nearly all metals and minerals showing a decided increase. This is especially noticeable in Portland cement, where the increase is from 3,584,586 barrels of 400 lbs. in 1898 to 5,805,620 barrels in 1899. Among the new products listed in recent years are ferromolybdenum, 6,000 lbs. in 1899; molybde-

num, 30,000 lbs.; tungsten, 45,000 lbs.; and Fuller's earth, 13,360 tons.

Among special articles of note are those on "Progress in the Aluminum Industry," by John B. C. Kershaw; "The Occurrence and Genesis of Californian Asphalt," by A. S. Cooper; "Notes on the Metallurgy of Bismuth," by W. Borchers; "Calcium Carbide," by John B. C. Kershaw; "The Hydraulic Cement Industry in the United States in 1899," by Frederick H. Lewis; "Notes on the Metallurgy of Chromium," by W. Borchers; "Notes on the Coarse Pottery Production of Great Britain," by Wilton P. Rix; "Fuel and Its Economical Utilization," by William Kent; "Progress in the Electrolytic Refining of Copper during 1899," by Titus Ulke; "Hofmann's Method for the Manufacture of Blue Vitriol," by Ottokar Hoffmann; "The Cutting and Polishing of Precious Stones," by Leopold Claremont; "Glass," by Robert Linton; "Rare Elements," by Victor Lenher; "The Electrolytic Production of Caustic Soda," by Alfred T. Weightman; "The Manufacture of Sulphuric Acid Stronger Than Chamber Acid," by F. J. Falding; and "The Sulphur Industry of Italy," by Giovanni Aichino.

This list is only a partial one. Many of the articles are illustrated, and not a few contain real contributions to the literature of the subjects treated.

E. H.

ANNALI DEL LABORATORIO CHIMICO CENTRALE DELLE GABELLE.
DIRETTI DEL DR. VITTORIO VILLAVECCHIA. VOL. IV. Roma Tipografia Elzeviriana, di Adelaide ved. Pateras. 1900. 528 pp.

The report of the Central Chemical Laboratory of the Italian Customs, Vol. IV, by Dr. Vittorio Villavecchia for the years 1898 and 1899 contains nineteen papers or reports on the methods of analysis or examinations of the character of manufactured articles and natural products which are of commercial importance to the country. They comprise the following.

1. "The Composition of Wines Imported into Italy during the Period from 1890-1897." V. Villavecchia.

2. "Methods for the Analysis of the Essential Oils of Bitter Fruits (Lemon, Orange, Bergamot)." G. Fabris. Contains interesting details of the methods of extraction as well as an account of the composition of the pure essences and the methods of detecting adulteration. The principal adulterant seems to be

oil of turpentine but the detection of its presence in small proportion does not seem very certain.

3. "Artificial Turpentine." G. Fabris.
4. "On the Analysis of Coal Tar and Its Preparations." G. Fabris.
5. "Contribution to the Analysis of Oils." M. Tortelli and R. Ruggieri.
 - I. The detection of cottonseed oil, oil of sesame, and peanut oil in olive oil.
 - II. The quantitative determination of peanut oil.
6. "A Method for Determining the Absolute Iodine Index of Fatty Substances." M. Tortelli and R. Ruggieri.
7. "The Oil and Wax (Vegetable Tallow) of the *Stellingia Sebifera*." M. Tortelli and R. Ruggieri.
8. "The Composition and Analysis of Vermouth." A. Bianchi.
9. "A Modification of Milliau's Test for the Presence of Cottonseed Oil." G. Armani.
10. "Boiled Vegetable Oils and Their Detection in Admixture with Other Oils." Tortelli and Ruggieri.
11. "The Quantitative Determination of Invert Sugar and Glucose in the Presence of Dextrine." A. Bianchi.
12. "The Determination of the Point of Solidification of Fatty Acids." R. Morischini.
13. "The Analysis and Composition of Certain Qualities of Commercial Bread." G. Fabris and D. Marino.
14. "On the Heating of Certain Gums Used in the Manufacture of Varnishes." G. Armani.
15. "The Characteristics and the Illuminating Power of Stearine, Paraffin, and Spermaceti Candles." R. Ruggieri.
16. "A Contribution to the Knowledge of the Distinctive Characteristics and the Illuminating Power of American Petroleum as Compared with the Russian." G. Rossi.
17. "The Chemical Analysis of Commercial Inks." G. Malagnini.
18. "A Study of the So-called Spices or Powdered Condiments of Commerce." S. Camilla.
19. "Artificial Silks and the Tests to Distinguish Them from Natural Silks." A. Salaro.

Most of these papers are interesting and valuable but from their nature they are difficult to abstract.

The number of samples examined in the laboratory in 1898 was 6,158; in 1897, 5,533. The majority of these consisted of beer, wine, and oils, but almost everything dutiable is represented.

ANDREW A. BLAIR.

(1) **EXPERIMENTAL CHEMISTRY.** BY L. C. NEWELL. 12 mo. xvi+410 pp. 114 illustrations. D. C. Heath & Co. Price, \$1.10.

(2) **THE ELEMENTS OF INORGANIC CHEMISTRY.** BY W. A. SHENSTONE. London: Edward Arnold. 12mo. xii + 506 pp. 142 illustrations.

(1) The purpose of this book, as the preface states, "is to promote the more efficient teaching of chemistry by modern methods. The choice and arrangement of subject-matter is based on the author's extended experience with students of varied ability. The book as a whole is the outcome of a desire to provide a course in chemistry which shall be a judicious combination of the inductive and deductive methods." Considerable care has been taken to eliminate errors since it appears from the preface that the entire MS. has been read by three other teachers of chemistry and the proof by fourteen.

Laboratory methods are given prominence—there are 201 experiments in all—and the interrogation point is freely used; some teachers will think too freely. Sixteen pages are included in the chapter on acids, bases, and salts and 25 under atoms, molecules, and related subjects. This latter chapter is open to serious criticism. The statements contained in it are well enough, but such topics as the methods for determining atomic weights, ions and ionization and applications of the theory of electrolytic dissociation, are out of place in a first book on chemistry. When teachers of chemistry learn not to give as a first course more than is necessary, and to follow this up by supplementary courses, we shall have better results. Shooting over the heads of students is still the most common fault in textbooks and teachers. The book is an excellent piece of work mechanically.

(2) Like the book noticed above this is evidently intended as a first book in chemistry. The author says: "I have endeavored to provide a book which begins with a course of experimental work for quite young students and develops at the later stages

into a text-book suitable for those who are older; that is, into a text-book containing fewer facts than those written solely for senior students." Part I contains a concise and well-written introduction treated under the captions: "The Chemistry of Fire; Gain of Weight and Combustion; Lavoisier's Researches on Combustion; Is Matter Indestructible? Can We Create It? and Principle of the Conservation of Mass." These topics are briefly treated and in language easily comprehended by a beginner and are illustrated by experiments to be performed by the student.

Chapters II and III contain an introductory study of water, illustrated by experiments which teach methods of determining melting- and boiling-points, the use of the barometer, fractional and destructive distillation, the pipette, specific gravity determinations, etc. Chapter IV tells how to dissolve, crystallize, the use of plotted curves to show solubility, the desiccator, etc. Chapter V treats of the electrolytic decomposition of water, the chemical elements, compounds and mixtures, synthesis, analysis, substitution, and double decomposition. Chapter VI continues the study of water and treats of water of crystallization, the nature of solution, the action of water with the metals, the composition of water by weight, the law of constant proportions, hydrogen peroxide, and the law of multiple proportions.

Chapter VII is a study of the atmosphere, combustion, flame, plants, and animals.

Part I as outlined above covers 94 pages and contains not a single symbol. In Part II chemical nomenclature is taken up and the rest of the book follows, in great measure, the ordinary line of treatment. Here again too much is given, but in other respects the book is a good piece of work and worth the careful study of teachers.

E. H.

AIR, WATER AND FOOD FROM A SANITARY STANDPOINT. BY ELLEN H. RICHARDS AND ALPHEUS G. WOODMAN. First edition. First thousand. New York: John Wiley & Sons. 1900. 226 pp. Price, \$2.00.

This is an extremely practical book dealing with the common problems of sanitary science in a simple yet thorough manner, and one can not read it through without being convinced that the authors know from their own observations what they are

writing about. After a brief general introduction we find 33 pages devoted to the study of the atmosphere, its general composition, usual contaminations, methods of ventilation, and methods of air analysis from the sanitary standpoint. Then follow, in 78 pages, 3 chapters on water in which many subjects besides those of analysis are discussed. Chapter V is supposed to be written from the "Householder's Standpoint," and Chapter VI from that of the chemist, but both may be read with interest and profit by persons who are not chemists and who have had no training in chemistry beyond that given in ordinary college courses. It is pleasing to see that the authors are not over-impressed with the importance of bacterial analysis in the practical investigations of water. Chapter VII contains a good collection of analytical methods and from the well-known experience of the authors in these matters it will prove valuable to those employed either as teachers of sanitary chemistry or as practical analysts.

The following 75 pages of the book deal with questions of food and partly from the popular standpoint. Many pertinent suggestions are made on the adulteration of common articles, and in the last chapters analytical methods are given by which the practical purity or value of a number of products may be determined. The book closes with a collection of tables, directions for making standard reagents, and with a bibliography of important books and papers dealing especially with topics discussed in the previous pages.

J. H. LONG.

ESSENTIALS OF MEDICAL AND CLINICAL CHEMISTRY WITH LABORATORY EXERCISES. BY SAMUEL E. WOODY, A.M., M.D. Fourth edition. Revised and enlarged. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1900. viii+235 pp.

In this book, as in many others of its class, we find an attempt to present what the author considers as the "essentials" of medical chemistry, so-called, within the limits of a single small volume. The space devoted to general and inorganic chemistry, with experiments and qualitative tests, amounts to 124 pages; organic chemistry takes up 47 pages, and clinical chemistry, covering urine analysis and the examination of milk, saliva, and gastric juice, 50 pages more. A very good index completes the book. The author has condensed a good deal of information

(not all of it quite accurate) within the rather narrow limits of the volume and it must be admitted that if the medical student should actually learn all that is there presented he would know much more than the average student carries away with him. But it seems to the present writer that the best selection of matter has not always been made, and that in his effort to be brief the author has very often sacrificed accuracy and clearness. Thus, we find as the definition of an alcohol the following, p. 144: "An alcohol is generally regarded as the hydrate of a hydrocarbon radical, since its formula always has a hydrocarbon radical at its positive end, and the radical HO at the negative end."

It is true that medical students can not devote a large portion of their time to the study of chemistry, but in the time they do spend in elementary chemistry their instruction should be as accurate and systematic as that given to students in the freshman or sophomore years of general colleges. It is a mistake to suppose that there is one kind of elementary chemistry for the clergyman, another for the lawyer, and a third (and the briefest of all) for the doctor. It is the present writer's opinion that the book before him does *not* contain the essentials which a medical man should know.

J. H. LONG.

AN OUTLINE OF THE THEORY OF THERMODYNAMICS. By EDGAR BUCKINGHAM, Associate Professor of Physics and Physical Chemistry in Bryn Mawr College, Bryn Mawr, Pa. xi + 205 pp. New York: The Macmillan Company, 1900. Cloth. Price, \$1.90.

This book is intended to bridge over the gap that exists between the ordinary text-books on thermodynamics and the modern memoirs on the subject. As the title indicates, special stress is laid on the theory, applications being introduced solely for the purpose of illustration. The subject is treated in 13 chapters, the topics considered being: Thermometry, Calorimetry, Material Systems in Thermodynamics, First Law, Principles of Thermochemistry, Calorimetric Properties of Fluids, Second Law, General Equations, Conditions of Thermodynamic Equilibrium, Thermodynamic Potentials, and Free Energy. One chapter is devoted to recapitulation and two to applications, while an appendix contains a list of useful books. The book is also provided with an index.

In treating his subject, the author begins with the explanation of simple fundamental concepts and gradually leads on to the more difficult relations involved; so that the book (though intended to bridge over a gap, as above stated) is yet complete in itself. The presentation is clear; and the student of thermodynamics will find the book a real aid in mastering the subject. The growing importance of thermodynamics in chemistry will insure for this volume a welcome on the part of chemists.

The work of the publishers is excellent.

LOUIS KAHLENBERG.

THE OIL CHEMISTS' HANDBOOK. BY ERASTUS HOPKINS, Chemist in charge of the U. S. Laboratories at Boston, Mass. New York: John Wiley & Sons. 8vo. Price, \$3.00.

This book gives, in a clear and concise form, the principal methods of testing the animal and vegetable fats, waxes, and oils, the mineral oils being considered only so far as they occur as adulterants.

A peculiar feature of the work is the tables of the properties and analytical constants of the oils; these have been selected with the greatest care from the original sources, the maximum, minimum, and mean values being given. Their arrangement is numerical; *i. e.*, in the table of the iodine value, the oil having the highest comes first, so with the other constants. These are especially valuable and convenient, as information is obtained at a glance which would take some time to find were it in the body of the book. It is, however, not exclusively a compilation but includes the results of years of practical experience. It seems to the reviewer that in some cases the original method has been adhered to, to the exclusion of the experience of others in the subject. For example the method of Livache is given, as detailed by him in 1886, without stating the experience of Weger and Lippert in 1898 and 1899. So too with regard to the Bechi test, the early procedure employing colza oil (which has since been shown to be unnecessary) is described without giving all the precautions shown to be needful to obtain reliable results; no results of later work are given. Regarding the determination of viscosity it would seem that the statement should have been made that for technical work the Saybolt,

Redwood, or Engler viscosimeter should be employed, rather than a pipette which is no longer much used.

In the matter of references the volume leaves something to be desired, many of the later being omitted, especially in connection with the iodine value. No mention could be found of the heat of bromination test for oils although the valueless sulphur chloride test is given; nor of Halphen's test for cotton-seed oil, one of the most reliable.

There are, too, certain errors of proof-reading and statement which are not in accord with the usual ideas; for example the use of 5.0 instead of 50.0 grams of oil (p 22) for the Maumené test; and in the tables the specific temperature reaction of Gill and Hatch does not refer to the Maumené test but to the heat of bromination test as will be seen from their article.¹ On p. 52. "All good cylinder oils are a mixture of fatty acids and mineral oils;" the cylinder oil should not contain free fatty acids, as most railroad specifications require "acidless animal oil." "Most blown oils are a mixture of fatty acid and mineral oils," being all that is stated about "blown oils," implies that mineral oil is a normal constituent instead of an occasional adulterant.

The tables, however, make the book very valuable and it will doubtless be found very useful to the trade and profession.

AUGUSTUS H. GILL.

BOOKS RECEIVED.

The Oil-Chemists' Handbook. By Erastus Hopkins, A.M., B.Sc. New York: John Wiley & Sons. 1900. viii + 72 pp. Price, \$3.00.

The Elements of Inorganic Chemistry, for Use in Schools and Colleges. By W. A. Shenstone, F.R.S. London: Edward Arnold. 1900. xii + 506 pp. Price, 4s., 6d.

Experimental Chemistry. By Lyman C. Newell, Ph.D. Boston: D. C. Heath & Co. 1900. xv + 410 pp.

Fruit Diseases and How to Treat Them. Bulletin No. 66. West Virginia Agricultural Experiment Station, Morgantown, W. Va. 38 pp.

Air, Water, and Food, from a Sanitary Standpoint. By Ellen H. Richards and Alpheus G. Woodman, Instructors in Sanitary Chemistry in Massachusetts Institute of Technology. New York: John Wiley & Sons; London: Chapman & Hall. 1900. 225 pp. Price, \$2.00.

The Volatile Oils. By E. Gildemeister and Fr. Hoffmann Translated

¹ This Journal, xi, 27.

by Edward Kremers. viii + 733 pp. Four maps and numerous illustrations. 1900. Milwaukee: Pharmaceutical Review Publishing Co. Price, \$5.00 net.

The Wellcome Chemical Research Laboratories, Established 1896. By Frederick B. Power, Ph.D., Director, 6 King St., Snow Hill, London, E. C. 18 pp.

The Question of Temperature-Influence on the Specific Rotation of Sucrose. By Ferdinand G. Wiechmann, Ph.D. 1900. 37 pp.

Nutrition Investigations at the California Agricultural Experiment Station, 1896-1898. By M. E. Jaffa, M.S. Bulletin No. 84. U. S. Department of Agriculture, Washington, D. C. 39 pp.

A Report of Investigations on the Digestibility and Nutritive Value of Bread. By Chas. D. Woods and L. H. Merrill, Maine Agricultural Experiment Station. Bulletin No. 85. U. S. Department of Agriculture, Washington, D. C. 1900. 51 pp.

Commercial Fertilizers. By H. A. Huston, State Chemist, Purdue University, Lafayette, Ind. Special Bulletin. August, 1900. 24 pp. Published by the author.

Elements of Mineralogy, Crystallography, and Blowpipe Analysis, from a Practical Standpoint, including a description of all common or useful minerals, the tests necessary for their identification, the recognition and measurement of their crystals, and a concise statement of their uses in the arts. By Alfred J. Moses, E.M., Ph.D., Professor of Mineralogy, Columbia University, and Charles Lathrop Parsons, B.S., Professor of General and Analytical Chemistry, New Hampshire College. New enlarged edition. viii + 414 pp., with 664 figures. New York: D. Van Nostrand Co. 1900. Price, \$2.00.

The Elements of Physics for Use in High Schools. By Henry Crew, Ph.D., Professor of Physics in Northwestern University. Second Edition, revised. New York: The Macmillan Co. 1900. xvi + 353 pp. Price, \$1.10.

The Laramie Cement Plaster. By E. E. Slosson and R. B. Mondy. Published as part of the Tenth Annual Report of the Wyoming College of Agriculture and Mechanics. Laramie, Wy. 1900. 18 pp.

Alkali Studies, V. By B. C. Buffum and E. E. Slosson. Published as part of the Tenth Annual Report of the Wyoming Experiment Station. Laramie, Wy. July, 1900.

Medical Legislation. Gov. Thomas' Veto of the Colorado Medical Bill. The Love Medical Bill of Ohio. Medical Ethics. Medical Talk Publishing Co., Columbus, Ohio. 16 pp. Price, 5 cents.

Bulletin No. 88. Commercial Fertilizers. August, 1900. 50 pp. Bulletin No. 89. Wheat. September, 1900. 24 pp. Kentucky Agricultural Experiment Station of the State College of Kentucky.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 53.]

THE PRODUCTION OF ALLOYS OF TUNGSTEN AND OF MOLYBDENUM IN THE ELECTRIC FURNACE.¹

BY CHARLES L. SARGENT.

Received September 27, 1900.

INTRODUCTION.

WITH the introduction of the electric furnace, the new field of chemistry at high temperatures was opened to investigation. Moissan especially succeeded in reducing the most refractory oxides, and in volatilizing many of them, as well as certain metals which were considered infusible. He described² a method of preparing alloys of vanadium, using the pentoxide as the source of vanadium.

Bernoulli³ prepared alloys of tungsten with copper, lead, bismuth, cobalt, nickel, etc. His method of working consisted in mixing the oxides of the two metals with lampblack, placing the mixture in a crucible and then heating it in an ordinary furnace. Proceeding in this manner he was not able to obtain alloys containing more than 10 per cent. of tungsten.

¹ From author's thesis presented for the degree of Doctor of Philosophy, University of Pennsylvania, 1900.

² "La Four Electrique," p. 246.

³ Pogg. Ann., III, 573.

Knowing the comparative ease with which tungsten and molybdenum are reduced from their oxides, it was thought that it might be possible to mix these oxides with oxides of other metals and then reduce the mixture in the electric furnace, obtaining as a final product an alloy of the two metals.

In the following experiments the furnace used was of the type known as the "Moissan." The carbon for the reduction was prepared by ignition of cane-sugar. The crucibles were made of graphite, modeled in the form of an assay scorifier. This shape is preferable, as it allows the arc to play directly on the bottom of the crucible. In some of the experiments the crucibles were lined with magnesia, thus preventing the hot metal from absorbing any of the graphite.

Unless otherwise mentioned the graphite crucibles were used. After each reduction the furnace was closed and allowed to cool before removing the crucible containing the fusion.

Ten preliminary experiments were made with tungstic acid, attention being paid more particularly to the influence of the carbon, and to the variation in voltage and amperage. The results showed that the amount of carbon used exerted a greater influence in the purity of the metal than variations in the strength of current, and the duration of its action. The product invariably contained carbon and traces of unreduced oxide. An effort was made to burn out the carbon by heating the impure metal in magnesia-lined crucibles, but the metal was changed to trioxide and magnesium was volatilized.

ALLOYS OF TUNGSTEN.

Tungsten trioxide and bismuthic oxide were mixed in varying amounts with carbon and exposed for several minutes to the action of a current of 60 to 80 volts, and 75 to 150 amperes. The quantity of bismuth detected in the metallic product in no case exceeded 0.64 per cent.

When cupric oxide was substituted for the bismuthic oxide, and a current of 75 to 150 amperes and 60 to 80 volts was applied for five minutes a regulus remained which showed, upon analysis, 18.24 per cent. of tungsten, 77.73 per cent. of copper, and 3.23 per cent. of carbon. On using a crucible lined with magnesia the copper was completely expelled and tungsten trioxide remained.

The results obtained in attempting to prepare an alloy of tungsten and manganese were negative. Two trials were made with chromium with the following conditions:

Experiment I.—

2 grams of tungsten trioxide	Voltage, 72-80.
2 " " chromic oxide	Amperage, 100-160.
2 " " carbon	Time, 5 minutes.

The reduction was made in a lime crucible. The resulting globule of metal was very hard and brittle, its surface being covered with a layer of chromic oxide. Its interior was gray in color. The specific gravity of the alloy equaled 8.96. It showed, upon analysis, 2.87 per cent. of chromium and 97.64 per cent. of tungsten.

Experiment II.—

2 grams of tungsten trioxide	Voltage, 72-85.
2 " " carbon	Amperage, 100-150.
1 gram of chromic oxide	Time, 5 minutes.

A carbon crucible was used in this experiment, but alloys containing a higher percentage of chromium than given in Experiment I, were not prepared. The next trial was made upon tungsten trioxide and cobaltic oxide with these conditions:

2 grams of tungsten trioxide	Voltage, 70-80.
2 " " cobaltic oxide	Amperage, 125-150.
1 gram of carbon	Time, 1 minute.

The crucible was of lime and the button, which was strongly magnetic, very tough and tenacious, had the specific gravity 10.96. Its analysis showed 51.86 per cent. of tungsten, and 48.26 per cent. of cobalt.

Upon varying the conditions to

1 gram of tungsten trioxide	Voltage, 65-70,
3 grams of cobaltic oxide	Amperage, 110-130,
2 grams of carbon	Time, 2 minutes,

and using, as before, a lime crucible the resulting metallic globule was discovered to be strongly magnetic, very tough, and it was broken with difficulty. Its specific gravity was found to be 8.92. Its analysis revealed the presence of 29.24 per cent. of tungsten, and 70.10 per cent. of cobalt.

The experiments conducted with the oxides of tungsten and nickel gave very favorable results :

Experiment I.

2 grams of tungsten trioxide	Voltage, 68-80.
2 " " nickel oxide	Amperage, 100-135.
2 " " carbon	Time, 2 minutes.

The reduction was made in a crucible lined with magnesia, and a globule was obtained which was slightly magnetic, could be filed, and was very tough. Its specific gravity equaled 10.66. Its analysis gave 50.22 per cent. of tungsten, and 49.88 per cent. of nickel.

Experiment II.—

3 grams of tungsten trioxide	Voltage, 75-90.
2 " " carbon	Amperage, 100-175.
1 gram of nickel oxide	Time, 1½ minutes.

The crucible was similar to that used in Experiment I. The resulting button was very hard and non-magnetic, extremely brittle, and easily pulverized. Its specific gravity equaled 12.66. The analysis showed 91.19 per cent. of tungsten, and 8.08 per cent. of nickel.

Repeated attempts were made to alloy tin and tungsten after the plan pursued with the other metals, but without success. It would, therefore, appear that starting with the oxides it is possible to prepare alloys of tungsten with those metals which require a high temperature for their volatilization. In the case of those requiring a low temperature, the oxide is apparently reduced and the metal driven off before the tungstic oxide is reduced. Doubtless alloys of tungsten and the lower fusing metals could be prepared by starting with the metals and melting them together; but if this is attempted in the electric furnace the intense heat drives off the lower-fusing metal, leaving the one with a higher fusing-point in the furnace.

ALLOYS OF MOLYBDENUM.

Three reductions of bismuthic oxide and tungsten trioxide were made :

Experiment I.—

4 grams of molybdenum trioxide	Voltage, 65-70.
4 " " bismuth oxide	Amperage, 90-120.
1 gram of carbon	Time, 2 minutes.

The resulting metal was very hard. Its specific gravity equaled 6.81. It gave, upon analysis, 91.61 per cent. of molybdenum, 6.50 per cent. of bismuth, and 2.28 per cent. of carbon.

Experiment II.—

2 grams of molybdenum trioxide	Voltage, 60-70.
8 " " bismuth oxide	Amperage, 75-110.
1.5 " " carbon	Time, 2 minutes.

A granular mass was obtained after heating for one and one-half minutes. It was re-fused for one minute in a crucible lined with magnesia, and was converted into a very hard metallic button, having a specific gravity of 8.91. It showed, upon analysis, 92 per cent. of molybdenum, 4.81 per cent. of bismuth, and 3.90 per cent. of carbon.

Experiment III.—

6 grams of molybdenum trioxide	Voltage, 70-80.
2 " " bismuth oxide	Amperage, 100-150.
1 gram of carbon	Time, 2 minutes.

A crucible with magnesia lining was used in this experiment. The analysis showed 97.91 per cent. of molybdenum, 1.10 per cent. of bismuth, and 1.21 per cent. of carbon. All efforts looking to the formation of a molybdenum-copper alloy were fruitless.

In the case of molybdenum and manganese the results were good and entirely unlike those observed with tungsten and manganese, as will be noticed in the following experiments :

Experiment I.—

4 grams of molybdenum trioxide	Voltage, 75-85.
4 " " manganese dioxide	Amperage, 100-150.
3 " " carbon	Time, 2 minutes.

A button, having a specific gravity of 7.08, was obtained. It gave, upon analysis, 71.07 per cent. of molybdenum, 14.36 per cent. of manganese, 9.60 per cent. of iron, and 4.34 per cent. of carbon. The iron in this alloy came from the manganese dioxide.

Experiment II.—

2 grams of molybdenum trioxide	Voltage, 70-80.
6 " " manganese dioxide	Amperage, 100-130.
3 " " carbon	Time, 2 minutes.

The resulting alloy had the specific gravity 6.9. Its analysis

revealed the presence of 60.08 per cent. of molybdenum, 21.11 per cent. of manganese, 16.64 per cent. of iron, and 2.99 per cent. of carbon. My experience with molybdenum and chromium is briefly summarized in the following experiments:

Experiment I.—

2 grams of molybdenum trioxide	Voltage, 70-90.
6 " " chromic oxide	Amperage, 100-150.
2 " " carbon	Time, 3 minutes.

A carbon crucible was used in the reduction. Molybdenum trioxide, unmixed with carbon, was placed in the bottom of the crucible, and upon this trioxide was introduced a mixture of chromic oxide, the balance of the oxide of molybdenum and carbon. The product of the fusion was hard and brittle. Its specific gravity was found to be 6.53. Its analysis showed the presence of 12.82 per cent. of molybdenum, 76.71 per cent. of chromium, 7.52 per cent. of iron, and 2.55 per cent. of carbon.

Experiment II.—

4 grams of molybdenum trioxide	Voltage, 70-80.
4 " " chromic oxide	Amperage, 90-130.
3 " " carbon	Time, 3 minutes.

The alloy, steel-gray in color, proved to be hard and brittle. Its specific gravity was found to be 7.65, and upon analysis it showed 39.96 per cent. of molybdenum, 53.24 per cent. of chromium, and 6.22 per cent. of iron with a trace of carbon. An alloy of tin and molybdenum was not obtained.

Several trials were made with molybdenum and nickel oxides, but only those will be introduced here which gave definite results:

Experiment I.—

2 grams of molybdenum trioxide	Voltage, 70-80.
4 " " nickel oxide	Amperage, 75-125.
2 " " carbon	Time, 2 minutes.

The crucible was lined with magnesia for this fusion. The metal obtained was very hard and brittle, non-magnetic, and had a specific gravity of 7.61. Upon analysis it gave 17.72 per cent. of molybdenum, 80.93 per cent. of nickel, and 1.63 per cent. of carbon.

Experiment II.—

4 grams of molybdenum trioxide	Voltage, 75-80.
2 " " nickel oxide	Amperage, 100-150.
2 " " carbon	Time, 1 minute.

The alloy was soft and easily filed. It was non-magnetic and its specific gravity was found to be 8.00. Its analysis showed 65.10 per cent. of molybdenum, and 34.72 per cent. of nickel.

Experiment III.—

4 grams of molybdenum trioxide	Voltage, 73-75.
2 " " nickel oxide	Amperage, 140-160.
2 " " carbon	Time, 1 minute.

A graphite crucible was used in the reduction. The alloy was hard, brittle, and non-magnetic. Its specific gravity equaled 8.88. Its analysis showed the presence of 50.20 per cent. of nickel, 42.48 per cent. of molybdenum, 3.05 per cent. of carbon, and 4.04 per cent. of silica. The silica probably came from the material used in the manufacture of the graphite crucible.

The reduction of mixed oxides of molybdenum and cobalt was not attended with the least difficulty; indeed, from the appended results it would seem that these particular metals alloy in almost any proportion:

Experiment I.—

2 grams of molybdenum trioxide	Voltage, 68-75.
4 " " cobaltic oxide	Amperage, 100-175.
2 " " carbon	Time, 1½ minutes.

The crucible had a magnesia lining. The alloy was very hard, tough, and magnetic. Its specific gravity equaled 7.32. Its analysis gave 17.06 per cent. of molybdenum, and 82.34 per cent. of cobalt.

Experiment II.—

3 grams of molybdenum trioxide	Voltage, 70-90.
3 " " cobaltic oxide	Amperage, 100-160.
2 " " carbon	Time, 1½ minutes.

The crucible was lined with magnesia. The alloy was very hard, tough, and magnetic. Its specific gravity equaled 6.44. Its analysis showed 35.64 per cent. of molybdenum, 62.91 per cent. of cobalt, and 1.79 per cent. of carbon.

Experiment III.—

3 grams of molybdenum trioxide	Voltage, 75-80.
3 " " cobaltic oxide	Amperage, 175-190.
2 " " carbon	Time, 1½ minutes.

In this experiment I used a graphite crucible, and obtained an alloy that was hard, slightly magnetic, very brittle, and easily pulverized. The specific gravity was 6.94. Its analysis gave 47.10 per cent. of molybdenum, and 52.30 per cent. of cobalt.

Experiment IV.—

4 grams of molybdenum trioxide	Voltage, 75-95.
2 " " cobaltic oxide	Amperage, 125-175.
2 " " carbon	Time, 1½ minutes.

The crucible was lined with magnesia. The alloy was very hard, brittle, and feebly magnetic, with a specific gravity of 7.14. Its analysis gave 54.57 per cent. of molybdenum, and 45.35 per cent. of cobalt.

Experiment V.—

4 grams of molybdenum trioxide	Voltage, 70-100.
2 " " cobaltic oxide	Amperage, 110-150.
2 " " carbon	Time, 1½ minutes.

Here I used a graphite crucible, placing the molybdc oxide in the bottom. The alloy was soft enough to be filed, but was brittle and slightly magnetic. The specific gravity was 6.55. It gave, upon analysis, 49.47 per cent. of molybdenum, and 50.86 per cent. of cobalt.

While tungsten and molybdenum ordinarily show many similarities in their reactions, we observe in the preceding experiments differences not wholly devoid of interest. Thus, while tungsten and bismuth did not yield an alloy, with molybdenum and bismuth definite products did result. The experiments with tungsten and copper were positive, but with molybdenum it seemed impossible to alloy copper. Both metals failed to unite with tin, and while this was true of tungsten with manganese, the latter metal and molybdenum combined with apparent readiness. Cobalt, chromium, and nickel, of the seven metals whose oxides were used with the oxides of tungsten and molybdenum, seemed to alloy with the greatest ease with the tungsten and

molybdenum, yielding products which, in the case of cobalt and nickel, may prove to possess a commercial technical value, if prepared in large amounts.

A METHOD FOR THE RAPID DETERMINATION OF CARBON IN STEEL.

BY ROBERT JOB AND CHARLES T. DAVIES.

Received September 25, 1900.

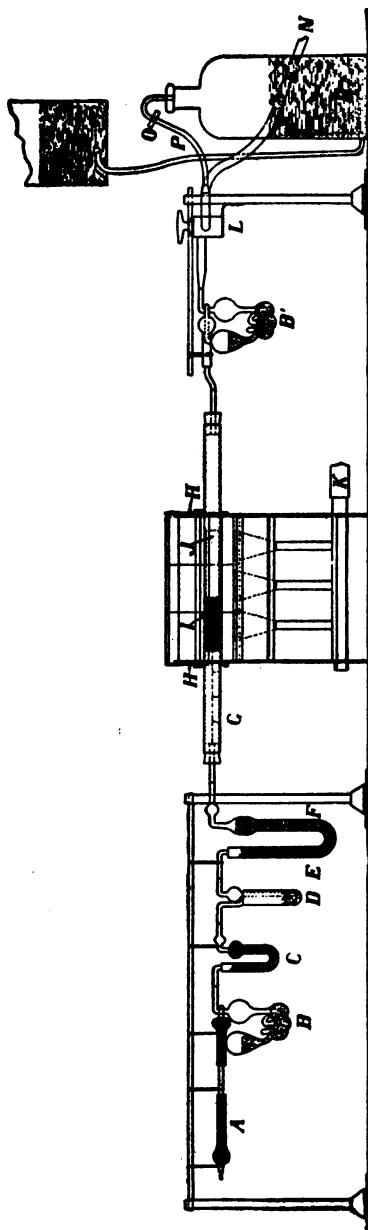
AFTER a very thorough trial of Dr. Sargent's apparatus for the rapid determination of carbon,¹ an investigation was begun with the object of retaining the continuous heating arrangement, and of reducing the apparatus to the simplest possible form without impairing in any way the accuracy of the results.

At the outset it was found that the separate, water-jacketed, copper oxide tube could be entirely eliminated by simply increasing the length of the combustion furnace to 9 inches, increasing the length of the porcelain combustion tube to 20 inches, and inserting closely rolled copper gauze about 4 inches in length, thoroughly oxidized prior to use, into the combustion tube, exactly as in the old method, placing pieces of clay-pipe stems between the copper oxide and the end of the tube in order to prevent the former from being forced out of place when the boat was run up against it in the determination.

Experiments with the furnace itself showed that three Bunsen burners each about $2\frac{1}{4}$ inches apart, having spreaders upon the tops, furnished sufficient heat to keep the porcelain tube at a bright red heat over 8 inches of its length. A thin sheet-iron shield was placed just beneath the tube as a protection from the direct action of the flame.

After the removal of the separate copper oxide tube, it was found that the gases, upon reaching the calcium chloride tube preceding the weighed bulbs, had been cooled to the temperature of the room, so that the condensing worm was no longer necessary, and further test after its removal proved that the excess of water remaining in the gas at that point was small, and was readily removed by the calcium chloride without necessity of frequent changing. It was further proved that the absorption

¹ This Journal, 22, 277.



of carbon dioxide in the bulbs was complete under these conditions, and that the temperature of the solution in the latter was not perceptibly raised, even upon very rapid running,—and also that moisture did not escape from the weighed potash bulbs and attached calcium chloride tube, even when the air was run at the rate of 8 bubbles per second, or faster than necessary to complete the combustion in twenty minutes.

Attention was next directed to the sand tube for the removal of chlorine and hydrochloric acid. Under certain conditions, and especially in very warm weather, it was found that the absorption by moist sand was incomplete, and thus that uniformly correct results could not be depended upon with this arrangement. Careful trial was therefore made of various absorbents both wet and dry, and we finally adopted the anhydrous cupric sulphate and cuprous chloride U-tube recommended by Blair, inserting beyond it a small bubble tube containing about 10 cc. of a saturated solution of silver sulphate in sulphuric acid of 1.40 specific gravity which served the double purpose of retaining any hydrochloric acid which might pass the U-tube, and of remedy-

ing the excessive dehydration produced by the copper salts.

The U-tube, E,F, is of the ordinary 6 inch form, and when filled contains cupric sulphate in the arm F, and cuprous chloride in E, both salts being freshly and thoroughly dehydrated, the copper sulphate being nearly white, and the cuprous chloride a dull brown. A small piece of glass wool is placed at the bottom of the tube to separate the salts, and also upon the top. The materials should be in granular form about $\frac{1}{4}$ inch in diameter, free from powder.

After once filling the tube it may be safely used without change until the copper sulphate on the top of the arm F becomes slightly blue or green, or until traces of hydrochloric acid begin to be caught in the silver sulphate solution. The tube should then be removed, placed upon the steam table, or otherwise heated, and a slow suction applied until the cupric sulphate has become nearly white. A second U tube is kept on hand ready for use and is inserted while the other is being dehydrated. Heating and aspirating for an hour will generally produce the proper dehydration, and the tube is then capped and hung up ready for use. As a general thing a large number of determinations may be made without changing the tube.

The silver sulphate bubble tube, D, is about $4\frac{1}{2}$ inches in height, and $\frac{7}{8}$ inch in diameter, holding about 25 cc., if full. When in use the tube contains from 5 to 10 cc. of the silver sulphate solution, this being blown in from a small wash-bottle. The tube is refilled after a determination if any precipitate has formed. This, however, seldom occurs unless the copper salts have become partially hydrated.

The calcium chloride tube, C, next to the silver sulphate tube retains the excess of moisture from the latter, and the gas passes into the potash bulbs in precisely the same degree of dryness as it emerges from the calcium chloride tube attached to the weighed bulbs, as shown by the fact that in the blank determinations there is almost invariably neither loss nor gain in the weight of the bulbs.

In filling the calcium chloride tubes care should be taken that the material be freshly dehydrated, and in granular pieces about $\frac{1}{4}$ inch in diameter and free from dust. The tubes should be filled as completely as possible, tapping lightly upon them and

filling close to the top, placing a very small piece of cotton at each end.

The potash bulbs, B and B', are practically the same as those recommended by Dr. Sargent, and hold, when filled for use, about 35 cc. of potassium hydroxide and weigh, including the calcium chloride, about 80 grams. These bulbs may be safely used until they have absorbed 2.5 grams carbon dioxide after which they should be cleaned out and refilled with fresh potash solution of 1.27 specific gravity. The calcium chloride tube, which is about $2\frac{1}{4}$ inches in length, and $\frac{1}{4}$ inch in diameter, should also be refilled with dehydrated material at the same time. The calcium chloride tube, C, immediately before the weighed bulbs, should be refilled in the same manner as soon as the material begins to appear slightly moist at the end nearest the silver sulphate tube. This will usually occur after about fifty determinations. The old calcium chloride when removed can be thoroughly dehydrated in a few minutes by heating in an iron or porcelain dish.

In the course of our work more or less difficulty was at first experienced owing to the cracking of the porcelain tube, especially so when the boats were not warmed before inserting. We found, however, that this could be completely remedied by putting into the combustion tube a piece of platinum foil bent into tubular form, and fitting the combustion tube closely, being careful to have the edges somewhat beveled so that the boat, when pushed in with the wire, would run up smoothly upon the foil, the object of the latter, being, of course, to withdraw the heat absorbed by the boat from a considerable area of the combustion tube instead of from a few points. The above was noted by Dr. Sargent in the paper above referred to.

Attention was next turned to the purity of the oxygen supply, in order to avoid the necessity for the preheating furnace. Investigation showed that commercial oxygen free from hydrocarbons could be readily obtained. Therefore, we merely stipulate with the order that the material shall be of this quality, and upon arrival of the tank run a blank determination, passing the oxygen for ten minutes and then the air in the usual manner. The final weight of the bulbs after forty minutes in the balance should not vary more than 0.2 of a milligram from the original weight. In case, however, a pure supply could not be obtained,

thus necessitating preheating of the gas, we found that a separate appliance could be avoided by simply passing a copper tube through the combustion furnace, utilizing the heat of the 3 burners for the purpose. An apparatus of this nature was attached readily to the furnace by boring two quarter-inch holes in each end of the furnace just above, and slightly to one side of the spreaders of the Bunsen burners, running a seamless copper tube of $\frac{1}{4}$ inch outside diameter entirely through the furnace, out through the end and back upon the opposite side parallel to the first, having the tube in such position that the flame would not play directly upon it, but still so close that the heat would bring it to redness. The ends of this tube, after passing through the furnace, were bent down almost to the level of the desk, and then extended along to the connection of the oxygen supply beyond the three-way cock, L. With this length of about 18 inches from the furnace, the ends of the copper remained cool under all conditions of service, and could thus be attached direct to the rubber tubes leading respectively to the oxygen and to the three-way cock, without any necessity for a water-cooling arrangement.

In the regular determinations we heat up the furnace by lighting the middle burner, turning up one-half for five minutes, then turning up full, at the same time turning up the two end burners one-half, and after five minutes giving the full flame. The tube will be red hot within fifteen minutes from the start, and ready for the day's determinations. If then a boat is in the tube it is pulled out with the wire hook quickly upon a porcelain tile, the weighed potash bulbs, after removing the capillary tips, are connected in position, and the oxygen started through the purifying bulbs, B', at the rate of about 4 bubbles per second. The determination boat is then removed from the oven, placed within the end of the tube and run quickly into position against the copper oxide with the wire, which is removed at once, and the gum stopper inserted. The oxygen is passed for seven minutes at the above rate, then shut off, and the three-way cock turned and air passed at the rate of about 6 or 7 bubbles per second for twelve and one-half minutes regulating the pressure as necessary by means of the clamp O, and passing about 1 liter of air. The stopper is then removed from the end of the tube,

the bulbs disconnected, and another set of previously weighed bulbs inserted and the second combustion proceeded with. Three weighed bulbs are used in running a set of determinations, and one of the same size but slightly lighter than the others is kept upon the opposite pan of the balances as a counterpoise. The weights are taken after letting the bulbs stand for forty minutes in the balances. The furnace remains hot throughout the day's work without attention.

As to accuracy of results with this apparatus, we have checked repeatedly upon various standard steels, and have obtained uniform and practically identical results with those obtained by the regular combustion method with a platinum tube.

In its present form the apparatus can be readily made by cutting down an old furnace; no water connections are required, the number of joints is reduced to a minimum, the cost of operation as well as the initial cost are greatly reduced below the cost of the old combustion method, a porcelain tube is as satisfactory and quick as a platinum tube, and the entire apparatus from end to end can be placed upon a table 5 feet long.

In this apparatus we have retained what seemed to be for our purpose the most desirable features of the various appliances now in use and wish to make due acknowledgment for them.¹

We have found it very advantageous to rechlorinate the double chloride of copper and potassium solution after Dr. Sargent's method.² As the solution gradually becomes neutral we find it desirable after rechlorinating to make addition of hydrochloric acid in sufficient amount to restore the original acidity, thus preventing the separation of salts, and increasing the rapidity of solution.

The acidity can be determined very easily by titrating 5 cc. of the rechlorinated solution with standard potassium hydroxide solution, taking as the end-reaction the point at which the ferric hydroxide just formed fails to go into solution after shaking. Titration is then made of 5 cc. of a solution of one part hydrochloric acid and 13 parts water (the normal acidity of the double chloride solution) with a drop of neutral ferric salt as indicator, the end-point being determined as above; comparison of the

¹ The potash bulbs and silver sulphate tube were made to order by Queen & Co.

² This Journal, 22, 210.

acidity of the two solutions with the volume of the solution rechlorinated will show the amount of hydrochloric acid needed.

LABORATORY OF THE PHILADELPHIA AND READING
RAILWAY COMPANY, READING, PA.,
September 13, 1900.

DETERMINATION OF IRON IN MAGNETITE ORE BY THE SPECIFIC GRAVITY TEST.¹

BY JOSEPH W. RICHARDS.

Received October 22, 1900.

MANY magnetite ores are simply mixtures of magnetite and quartz. The dressing of such ores at the mines up to a salable percentage of iron is often an important matter, and in such cases the weight of the ore, as determined by its "feel," is the determining factor as to whether it should pass into the ore pile or to the dump. Every new streak of ore opened up brings new material to be thus classified. For such classification, the specific gravity of the ore, carefully taken on a good pair of scales, is of quite sufficient accuracy to answer all practical purposes. Indeed, in many cases, considering the difficulty of obtaining a small representative sample from a mixed lot of ore such as the chemist requires, the specific gravity test made on a considerable weight of sample pieces may be quite as satisfactory as an analysis. The various ways in which specific gravity may be practically determined on an ordinary good scale need not be discussed here; anywhere from 1 to 50 pounds of ore may be tested, according to the scale at hand, and the accuracy desired, and results usually obtained accurate to 0.10 in any case, and often to 0.02 or 0.03, in the specific gravity. Such variations would mean a variation of 1 to 3 per cent. on the iron content, according to the richness of the ore. With ores over 45 per cent. of iron, the variation or error need not be over 2 per cent. on the iron, in any case.

To facilitate such tests, I have calculated the following table of the specific gravity of mixtures of magnetite and silica, of specific gravity of 5.18, and 2.66 respectively, for every 1 per cent. of iron contained, giving in each case also the percentages of magnetite and quartz in the mixture, the latter datum being of particular importance in valuing the ore.

¹ Read at the October meeting of the Lehigh Valley Section of the American Chemical Society.

Fe. Per cent.	Fe ₂ O ₄ . Per cent.	SiO ₂ . Per cent.	Specific gravity.	Fe. Per cent.	Fe ₂ O ₄ . Per cent.	SiO ₂ . Per cent.	Specific gravity.
0	0.0	100.0	2.66	37	51.0	49.0	3.54
1	1.4	98.6	2.67	38	52.4	47.6	3.57
2	2.8	97.2	2.69	39	53.8	46.2	3.60
3	4.1	95.9	2.71	40	55.2	44.8	3.64
4	5.5	94.5	2.73	41	56.6	43.4	3.67
5	6.9	93.1	2.75	42	58.0	42.0	3.70
6	8.3	91.7	2.77	43	59.4	40.6	3.74
7	9.7	90.3	2.79	44	60.8	39.2	3.77
8	11.0	89.0	2.81	45	62.1	37.9	3.81
9	12.4	87.6	2.83	46	63.5	36.5	3.85
10	13.8	86.2	2.85	47	64.9	35.1	3.89
11	15.2	84.8	2.87	48	66.3	33.7	3.93
12	16.6	83.4	2.89	49	67.7	32.3	3.97
13	18.0	82.0	2.92	50	69.1	30.9	4.01
14	19.3	80.7	2.94	51	70.5	29.5	4.05
15	20.7	79.3	2.96	52	71.8	28.2	4.09
16	22.1	77.9	2.98	53	73.2	26.8	4.13
17	23.5	76.5	3.00	54	74.6	25.4	4.17
18	24.8	75.2	3.03	55	76.0	24.0	4.22
19	26.2	73.8	3.05	56	77.4	22.6	4.26
20	27.6	72.4	3.07	57	78.8	21.2	4.31
21	29.0	71.0	3.09	58	80.1	19.9	4.36
22	30.4	69.6	3.12	59	81.5	18.5	4.41
23	31.8	68.2	3.14	60	82.9	17.1	4.46
24	33.2	66.8	3.17	61	84.2	15.8	4.51
25	34.5	65.5	3.20	62	85.6	14.4	4.56
26	35.9	64.1	3.22	63	87.0	13.0	4.61
27	37.3	62.7	3.25	64	88.4	11.6	4.66
28	38.7	61.3	3.27	65	89.8	10.2	4.72
29	40.0	60.0	3.30	66	91.2	9.8	4.78
30	41.4	58.5	3.33	67	92.6	7.4	4.84
31	42.8	57.2	3.36	68	94.0	6.0	4.90
32	44.2	55.8	3.39	69	95.3	4.7	4.96
33	45.6	54.4	3.42	70	96.7	3.4	5.02
34	47.0	53.0	3.45	71	98.0	2.0	5.09
35	48.3	51.7	3.48	72	99.4	0.6	5.16
36	49.7	50.3	3.51	72.4	100.0	0.0	5.18

LEHIGH UNIVERSITY,
October 18, 1900.

IRREGULAR DISTRIBUTION OF SULPHUR IN PIG IRON.

BY RANDOLPH BOLLING.

Received October 8, 1900.

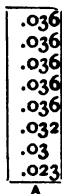
SULPHUR determinations sometimes show marked differences when samples are drilled from different points on the same pig. M. J. Moore¹ has noticed the low results obtained from

¹ This Journal, 21, 972-975.

"shot samples" as compared with those cast in sand. He states that the results obtained from the "shot samples" are low as compared with the gravimetric determinations. Moore used the volumetric method on his sand and shot samples.

The variations between sulphur determinations, made on drillings from the lower surface of the pig, and those made on the upper surface have been frequently noticed here, and in some cases have been so marked that a cast which was drilled from the top surface of the sample pig, on analysis, showed 0.075 per cent. sulphur, and consequently graded as "off basic" (sulphur running over 0.05 per cent.) was found to be "basic" when the drillings were taken by drilling a hole entirely through the pig; the second determination showed 0.045 per cent. sulphur.

To study the irregular distribution of sulphur a rod 12×14 inches was cast in sand by collecting a pound or so at intervals from the runner as a cast was being made until about 10 pounds had been ladled out, and then poured into the mold. This was then drilled at regular intervals of $1\frac{1}{8}$ inches; in all 8 holes were drilled. Sulphur was determined by the cadmium chloride method. The figure represents a cross-section of the rod reduced to a small scale. Beginning at bottom of the rod at the point marked A, the decimal points will indicate where the drill entered. The percentages of sulphur it will be noticed are lower at the bottom of the mold than at the top.



It will be seen that the difference between the upper and lower surface amounts to 0.013 per cent., and it would therefore be wrong to report a determination made on drillings taken either at the top or bottom; and to obtain a representative sample it would be necessary to drill a hole entirely through the sample pig, and mix the drillings well before making the determination. By this procedure a fairly average sample would be obtained.

LABORATORY VIRGINIA IRON, COAL, AND
COKE CO., BUENA VISTA, VA.

THE COMPOSITION AND ANALYSIS OF LONDON PURPLE.

BY J. K. HAYWOOD.

Received October 22, 1900.

LONDON purple has, up to the present time, been supposed to consist mainly of calcium arsenite and an organic dye residue. From the work which will appear later on in this article, however, it is shown that the arsenic in London purple is principally in the "ic" condition, so that it consists mainly of calcium arsenate, calcium arsenite, and an organic dye residue. On account of the method of manufacture, as I have mentioned in an earlier paper,¹ some of the arsenic will nearly, or quite, always appear in the free condition. It will thus be seen that an analysis of London purple would include the determination of moisture, total arsenic acid, total arsenious acid, soluble arsenic acid, soluble arsenious acid, calcium, and sand.

DETERMINATION OF MOISTURE.

The moisture of London purple, was determined by drying at 100° for from twelve to fifteen hours. On four samples (A, B, C, and D) examined by me the results were:

	A.	B.	C.	D.
	Per cent.	Per cent.	Per cent.	Per cent.
Moisture	1.87	4.07	2.76	2.73

DETERMINATION OF TOTAL ARSENIC.

As regards the determination of total arsenic, it will at once be seen that on account of the presence of the organic dye-stuff residue, and of the calcium, the same methods cannot be applied as those mentioned in my earlier paper for Paris and Scheele greens.

I therefore tried to apply to London purple the same method for determining total arsenic as is used for determining phosphoric acid in phosphates, namely:

1. About 0.5 gram of the sample was oxidized with fuming nitric acid, the excess removed by evaporation, molybdate

¹ "Adulteration and Analysis of the Arsenical Insecticides." This Journal, 22, 56.

solution added and the yellow precipitate carefully washed, and afterwards dissolved in ammonia, magnesium mixture added and the arsenious oxide weighed as magnesium pyroarsenate ($\text{Mg}_2\text{As}_2\text{O}_7$). In carrying out this method, however, I found that the fuming nitric acid did not oxidize all of the organic dye-stuff and that consequently all of the yellow molybdate precipitate did not come down. As the results obtained showed that the amount of arsenious oxide was about 10 per cent. below that which I subsequently found to be present, the method was abandoned.

2. I next tried to determine the total arsenic by dissolving the purple in hydrochloric acid, precipitating with hydrogen sulphide, washing, dissolving in ammonia, reprecipitating with hydrochloric acid, washing first with water, then, after drying, with carbon disulphide, and finally weighing as arsenious sulphide. The arsenious sulphide obtained, however, was perfectly black, from contamination with organic matter, hence this method was also abandoned.

3. The next method which I tried was as follows:

About 2 grams of the sample were dissolved in hydrochloric acid (1 : 4) and heated to from 60° – 70° C. to get all arsenic in solution (not higher for fear of driving off arsenious chloride). The solution was then filtered to a definite volume, an aliquot portion taken for analysis and the arsenic precipitated by hydrogen sulphide at 70° C. The precipitate was separated by filtration, washed, and finally both filter and precipitate oxidized with fuming nitric acid in a small flask. After all sulphur and organic matter appeared to be oxidized, the solution was evaporated to a small volume, filtered, treated with magnesia mixture prepared according to the Austin formula,¹ and then with a little ammonia. After settling a few hours the precipitate was washed with ammonia water (1 cc. ammonia to 100 cc. of water) on a Gooch crucible, dried, and the Gooch crucible placed in a solid platinum crucible where it was ignited by degrees in the ordinary way.

Employing this method, the following results were obtained on the four samples (A, B, C, and D) :

¹ *Ztschr. anorg. Chem.*, 23, Heft. 2.

	A.	B.	C.	D.
	Per cent.	Per cent.	Per cent.	Per cent.
Arsenious oxide.....	35.50	37.48	36.47	35.90

Another sample, X, gave results in triplicate, as follows :

Per cent.

33.53

33.32

33.79

Although this method seemed to give fairly good results, I did not feel satisfied for two reasons, namely :

1. The magnesium ammonium arsenate was always dark-colored, showing that the nitric acid had not oxidized all the organic matter, and that consequently when the precipitate was ignited, there would be a loss of arsenic.

2. From the length of time necessary to precipitate the arsenious sulphide (As_2S_3), it appeared to me that some of it at any rate must be in the "ic" condition, and that consequently a method should be employed which would differentiate between the "ous" and "ic" arsenic.

With these two points in view I worked out a method modeled after the Thorn Smith method, mentioned in my earlier paper, but quite different in all of the small details. It is as follows :

3. Two grams of London purple were dissolved in about 80 cc. of water, and 20 cc. of hydrochloric acid at a temperature of from 60° to 70° , just as in the method above described, filtered, and washed to a volume of 300 cc. One hundred cc. of this was treated in a 500 cc. flask with sodium bicarbonate in excess. The contents of the flask were then brought to the mark with water, using a few drops of ether to destroy bubbles, and 250 cc. filtered off. To this was added starch solution, and the standard iodine solution, until the blue color appeared. The result was the arsenious oxide as such, in 50 cc. of the original solution.

Again 50 cc. of the original solution (representing 0.33333 gram) was heated to 80° on the water-bath, and then taken off and 50 cc. of hydrochloric acid, and three grams of potassium iodide added. The mixture was allowed to stand for at least fifteen minutes, the "ic" arsenic thus being reduced to "ous" arsenic by the action of the potassium iodide, in the acid solution,

iodine being set free. The solution was then rinsed out in a large beaker, and tenth-normal sodium thiosulphate added, drop by drop, to get rid of the iodine. The end-point here was rather difficult to read on account of the very dark color of the solution, but with a little practice one could determine it very easily, by proceeding as follows:

The sodium thiosulphate was run in a little at a time and occasionally a drop of the solution was added to a drop of starch paste. This would of course give a blue color with the starch, which became fainter and fainter as the iodine was used up. Finally when a drop of the solution only gave the slightest blue color, with the starch, a little starch paste was added directly to the whole solution, and the blue color dissipated with a few drops of thiosulphate. With a little practice one could in this way get the exact end-point every time. The solution was immediately made alkaline with solid sodium carbonate. It was again made slightly acid with hydrochloric acid, taking care that all of the solid particles of the sodium carbonate on the bottom were neutralized by the acid,¹ and finally made alkaline with sodium bicarbonate. Starch paste was now added and tenth-normal iodine until the blue color appeared. This end-point is easily read if the beaker is placed on a white surface between the eye and the light, and iodine run in until a distinct purple color appears. The figure thus obtained gave the total amount of arsenic in the solution as arsenious oxide. Subtracting the first figure from this we have the amount of arsenious oxide corresponding to arsenic oxide in 50 cc. of the original liquid. Working in this way I obtained the following results on the samples (A, B, C, and D).

Sample.	Arsenious oxide as such.	Total arsenious oxide present.	Arsenious oxide corresponding to arsenic oxide.	Arsenic oxide present.
	Per cent.	Per cent.	Per cent.	Per cent.
A	8.16	37.21	29.05	33.77
	8.16	37.21	29.05	33.77
	...	36.78	28.62	33.26

¹ If all of the sodium carbonate is not used up, it will itself act on the standard iodine subsequently to be added.

Sample.	Arsenious oxide as such. Per cent.	Total arsenious oxide present. Per cent.	Arsenious oxide corresponding to arsenic oxide. Per cent.	Arsenic oxide present. Per cent.
B	17.45	39.97	22.67	26.34
	17.16	40.12	22.82	26.50
	40.26	22.96	26.66
C	10.47	38.67	28.20	32.76
	10.47	38.81	28.34	32.93
D	6.40	37.07	30.67	35.62
	6.40	36.92	30.52	35.45
	...	37.21	30.81	35.79

It will thus be seen that this method not only allows of a determination of the arsenious oxide and the arsenic oxide but also gives very good duplicate results, which results are higher than those obtained by the previous methods. One would expect this on account of the loss which very likely takes place in the last method when the magnesium ammonium arsenate is burned in the presence of some organic matter, which has not been removed by the fuming nitric acid.

DETERMINATION OF CALCIUM OXIDE.

In order to determine calcium oxide in London purple, a portion was dissolved in hydrochloric acid (an aliquot portion of the 300 cc. used in the determination of arsenious and arsenic oxides above would do), and hydrogen sulphide passed through. The precipitate was well washed, the filtrate evaporated to small bulk and transferred to a 200 cc. flask, when it was treated with ammonia (to precipitate the iron, etc.) and made to the mark. A 100 cc. portion of this was filtered off and treated with ammonium oxalate in the usual way. In this manner the following results were obtained on the samples (A, B, C, and D).

Samples.	Calcium oxide. Per cent.
A	25.09
B	23.59
C	24.55
D	25.03
On a fifth sample, X, triplicate results were..	<div> 23.25 23.25 23.40 </div>

DETERMINATION OF SOLUBLE ARSENIOS OXIDE.

To determine the soluble arsenious oxide, the same methods were used as those described in my previous paper for Paris and Scheele greens.¹ On a fifth sample, X, the results were as follows:

Method 1. Washing on the filter not tried.

Method 2. Extracting 1 gram with 500 cc. of water for a number of days at room temperature, and determining arsenious oxide by standard iodine in an aliquot portion of the filtrate.

Sample.	Time.	Arsenious oxide extracted.
		Per cent.
X.....	5 days	7.29
	10 days	7.88
	19 days	7.88

Method 3. Extracting 1 gram with successive portions of water at 50°-60° C.

Time.	Arsenious oxide extracted.
	Per cent.
1 day.....	7.78
2 days.....	$7.78 + 1.65 = 9.43$
3 days.....	$9.43 + 0.87 = 10.30$
4 days.....	$10.30 + 0.49 = 10.79$
5 days.....	$10.79 + 0.39 = 11.18$
6 days.....	$11.18 + 0.29 = 11.47$
7 days.....	$11.47 + 0.19 = 11.66$
8 days.....	$11.66 + 0.24 = 11.90$
9 days.....	Still gaining.

It will be seen from this that the only method which gave constant results was Method 2, above, just as in the case of Paris and Scheele greens. Applying this method to Samples A, B, C, and D, the following results were obtained:

Sample Nos.	Soluble arsenious oxide.
	Per cent.
A	2.43
B	13.3
	13.60
C	3.88
D	1.44

DETERMINATION OF SOLUBLE ARSENIC OXIDE.

To determine the soluble arsenic oxide, an aliquot portion of

¹ "Adulteration and Analysis of the Arsenical Insecticides." This Journal, 22, 568.

the liquid from Method 2 above, for soluble arsenious oxide (say 200 cc.), was transferred to a flask, made slightly alkaline with NaOH, and evaporated to about 25 cc. on a hot plate. The flask was then removed and allowed to cool to about 80°, and an equal volume of concentrated hydrochloric acid and 3 grams of potassium iodide added. It was allowed to stand fifteen minutes, the iodine set free, exactly used up with tenth-normal thiosulphate (the end-point is easily read without the use of starch), and the solution neutralized with sodium carbonate. It was again made slightly acid with hydrochloric acid, taking care that all lumps of sodium carbonate were acted on, then made alkaline with an excess of sodium bicarbonate, and titrated with iodine, using starch as an indicator. From this figure was subtracted the figure representing the amount of soluble arsenious oxide, and the remainder was calculated as arsenic oxide.

Proceeding in this way I obtained the following results :

Sample.	Soluble arsenic oxide. Per cent.
A	15.81
B	7.12
C	12.56
D	19.56

DETERMINATION OF SOLUBLE CALCIUM OXIDE.

In Method 2 above for soluble arsenious oxide and arsenic oxide, I also determined the per cent. of calcium oxide that had been dissolved by the action of the 500 cc. of water. The results on the samples (A, B, C and D) were as follows :

Sample.	Calcium oxide dis- solved by 500 cc. of water. Per cent.
A	7.80
B	6.60
C	7.00
D	10.80

DETERMINATION OF OTHER INORGANIC MATTERS.

The inorganic matter, insoluble in hydrochloric acid, mostly consisting of sand, was determined by dissolving the London purple in hydrochloric acid, filtering, washing, and burning the

COMPOSITION AND ANALYSIS OF LONDON PURPLE. 807

filter and contents. The results obtained on the samples (A, B, C and D) were as follows:

Sample.	Sand. Per cent.
A	3.54
B	2.61
C	2.46
D	3.55

The following is a condensed statement of the work done:

Sample.	Water. Per cent.	Sand. Per cent.	Total arsenic ¹ calculated as As ₂ O ₃ .		Total arsenious oxide as such. Per cent.	Total arsenic oxide as such. Per cent.	Total calcium oxide. Per cent.
			Precipitating as arsenious sulphide, oxidizing with nitric acid. (3) Per cent.	Volumetric iodine method. (4) Per cent.			
A	1.87	3.54	35.50	37.07	8.16	33.60	25.09
B	4.07	2.61	37.48	40.12	17.31	26.50	23.59
C	2.76	2.46	36.47	38.74	10.47	32.84	24.55
D	2.73	3.55	35.90	37.07	6.40	35.62	25.03
X	33.55	23.30

Sample.	Soluble arsenious oxide.		Soluble arsenic oxide, extracting with 500 cc. cold water. Per cent.	Soluble calcium oxide. Per cent.
	Method 2, extraction with 500 cc. cold water. Per cent.	Method 3, extraction with successive portions of water at 60-70°. Per cent.		
A	2.43	15.81	7.80
B	13.49	7.12	6.60
C	3.88	12.56	7.00
D	1.44	19.56	10.80
X	7.88	11.90

FORM IN WHICH VARIOUS CONSTITUENTS APPEAR.

Knowing the full inorganic composition of the four samples given above, we are now in a position to determine the form in which they appear in London purple. The calculation is very simple. If we subtract the soluble arsenious oxide from the

¹ Methods 1 (precipitating with molybdate) and 2 (weighing as arsenious sulphide) were abandoned as unsatisfactory.

total arsenious oxide as such, the soluble arsenic oxide from the total arsenic oxide as such, and the soluble calcium oxide from the total calcium oxide, we have left the insoluble arsenious oxide, the insoluble arsenic oxide, and the insoluble calcium oxide. If the form in which these are united is the normal calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$, and the normal calcium arsenite, $\text{Ca}_3(\text{AsO}_3)_2$, then the sum of the amounts of calcium oxide, necessary to unite with all the insoluble arsenious oxide to form calcium arsenite, and all of the insoluble arsenic oxide to form calcium arsenate, should be equal to the insoluble calcium oxide as determined.

We will now take up each of the samples and see if such is the case.

$$\begin{array}{lll} A. \text{ Total As}_2\text{O}_3 = 8.16 & \text{Total As}_2\text{O}_5 = 33.60 & \text{Total CaO} = 25.09 \\ \text{Soluble As}_2\text{O}_3 = 2.43 & \text{Soluble As}_2\text{O}_5 = 15.81 & \text{Soluble CaO} = 7.80 \end{array}$$

$$\text{Insoluble As}_2\text{O}_3 = 5.73 \quad \text{Insoluble As}_2\text{O}_5 = 17.79 \quad \text{Insoluble CaO} = 17.29$$

$$\text{As}_2\text{O}_3 : 3 \text{ CaO} :: 5.73 : x$$

$$x = 4.86 = \text{CaO necessary to form Ca}_3(\text{AsO}_3)_2$$

$$\text{As}_2\text{O}_5 : 3 \text{ CaO} :: 17.79 : x$$

$$x = 12.99 = \text{CaO necessary to form Ca}_3(\text{AsO}_4)_2$$

$$12.99 + 4.86 = 17.85 = \text{CaO theoretically necessary to form}$$

$$\text{Ca}_3(\text{AsO}_3)_2 \text{ and } \text{Ca}_3(\text{AsO}_4)_2$$

$$17.29 = \text{CaO actually found.}$$

$$\begin{array}{lll} B. \text{ Total As}_2\text{O}_3 = 17.31 & \text{Total As}_2\text{O}_5 = 26.50 & \text{Total CaO} = 23.59 \\ \text{Soluble As}_2\text{O}_3 = 13.49 & \text{Soluble As}_2\text{O}_5 = 7.12 & \text{Soluble CaO} = 6.60 \end{array}$$

$$\text{Insoluble As}_2\text{O}_3 = 3.82 \quad \text{Insoluble As}_2\text{O}_5 = 19.38 \quad \text{Insoluble CaO} = 16.99$$

$$\text{As}_2\text{O}_3 : 3 \text{ CaO} :: 3.82 : x$$

$$x = 3.28 = \text{CaO necessary to form Ca}_3(\text{AsO}_3)_2$$

$$\text{As}_2\text{O}_5 : 3 \text{ CaO} :: 19.38 : x$$

$$x = 14.15 = \text{CaO necessary to form Ca}_3(\text{AsO}_4)_2$$

$$14.15 + 3.28 = 17.43 = \text{CaO theoretically necessary to form}$$

$$\text{Ca}_3(\text{AsO}_3)_2 \text{ and } \text{Ca}_3(\text{AsO}_4)_2$$

$$16.99 = \text{CaO actually found.}$$

$$\begin{array}{lll} C. \text{ Total As}_2\text{O}_3 = 10.47 & \text{Total As}_2\text{O}_5 = 32.84 & \text{Total CaO} = 24.55 \\ \text{Soluble As}_2\text{O}_3 = 3.88 & \text{Soluble As}_2\text{O}_5 = 12.56 & \text{Soluble CaO} = 7.00 \end{array}$$

$$\text{Insoluble As}_2\text{O}_3 = 6.59 \quad \text{Insoluble As}_2\text{O}_5 = 20.28 \quad \text{Insoluble CaO} = 17.55$$

$$\begin{aligned}
 & \text{As}_2\text{O}_3 : 3\text{CaO} :: 6.59 : x \\
 & x = 5.59 = \text{CaO necessary to form Ca}_3(\text{AsO}_3)_2 \\
 & \text{As}_2\text{O}_3 : 3\text{CaO} :: 20.28 : x \\
 & x = 14.81 = \text{CaO necessary to form Ca}_3(\text{AsO}_4)_2 \\
 & 5.59 + 14.81 = 20.40 = \text{CaO theoretically necessary to form} \\
 & \quad \text{Ca}_3(\text{AsO}_3)_2 \text{ and Ca}_3(\text{AsO}_4)_2 \\
 & 17.55 = \text{CaO actually found.}
 \end{aligned}$$

D. Total $\text{As}_2\text{O}_3 = 6.40$	Total $\text{As}_2\text{O}_3 = 35.62$	Total $\text{CaO} = 25.03$
Soluble $\text{As}_2\text{O}_3 = 1.44$	Soluble $\text{As}_2\text{O}_3 = 19.56$	Soluble $\text{CaO} = 10.80$
<hr/>		
Insoluble $\text{As}_2\text{O}_3 = 4.96$	Insoluble $\text{As}_2\text{O}_3 = 16.06$	Insoluble $\text{CaO} = 14.23$
$\text{As}_2\text{O}_3 : 3 \text{ CaO} :: 4.96 : x$		
$x = 4.21 = \text{CaO necessary to form Ca}_3(\text{AsO}_3)_2$		
$\text{As}_2\text{O}_3 : 3 \text{ CaO} :: 16.06 : x$		
$x = 11.73 = \text{CaO necessary to form Ca}_3(\text{AsO}_4)_2$		
$4.21 + 11.73 = 15.94 = \text{CaO theoretically necessary to form Ca}_3(\text{AsO}_3)_2 \text{ and Ca}_3(\text{AsO}_4)_2$		
$14.23 = \text{CaO actually found.}$		

On another sample E the results were as follows :

$$\begin{aligned}
 & 10.91 = \text{CaO theoretically necessary to form Ca}_3(\text{AsO}_3)_2 \text{ and} \\
 & \quad \text{Ca}_3(\text{AsO}_4)_2 \\
 & 10.21 = \text{CaO actually found.}
 \end{aligned}$$

It will be seen from the above calculations that the amounts of calcium oxide, arsenious oxide, and arsenic oxide are such in Samples A, B, and E as to closely approximate the formulas $\text{Ca}_3(\text{AsO}_3)_2$ and $\text{Ca}_3(\text{AsO}_4)_2$. In Samples C and D the amounts of these three substances do not so closely approximate the formulas $\text{Ca}_3(\text{AsO}_3)_2$ and $\text{Ca}_3(\text{AsO}_4)_2$, but show there is a tendency to form compounds in which the amount of lime is less in proportion to the arsenious and arsenic oxides as in CaHAsO_4 and $\text{Ca}_2\text{As}_2\text{O}_5$.

I am inclined to believe from this work that the lime, arsenious and arsenic oxides in London purple are *usually* combined as the normal calcium arsenite and arsenate, but that sometimes small quantities of calcium arsenite and arsenate are formed in which the lime is less in proportion to the arsenious and arsenic oxides as in CaHAsO_4 and $\text{Ca}_2\text{As}_2\text{O}_5$. The factors that determine this are very likely the time of boiling, the original concentration of the liquor, the presence or absence of an excess of lime and the form in which the arsenic is present in the original dye residue.

DETECTION OF FOREIGN COLORING-MATTER IN SPIRITS.

[SECOND METHOD.]

BY C. A. CRAMPTON AND F. D. SIMONS.

Received October 29, 1900.

A method for the detection of caramel in spirits and vinegar, based upon the selective absorption of caramel coloring-matter by fullers' earth, was published by us in this Journal.¹ Since that time the method has given very satisfactory results in this laboratory in the examination of samples suspected of being artificially colored. the chief difficulty encountered in its application being the variable quality and color-absorbing power of fullers' earth as found in the market. This difficulty was partially overcome by obtaining a supply of the material, of uniform color-absorbing capacity to the degree best suited to the purpose in hand, and in quantity sufficient for a very great number of tests, so that it will not be necessary to change the standards for a long time to come.

We have lately perfected, however, a much more satisfactory and convenient test, which is based simply and solely upon the insolubility in ether of the coloring-matter of caramel and prune juice, the only foreign coloring materials known by us to be used for the artificial coloring of spirits. The coloring-matter of oak wood, on the other hand (principally flavescin), is soluble in ether, which readily removes it from its solution in water or alcohol when shaken with it.

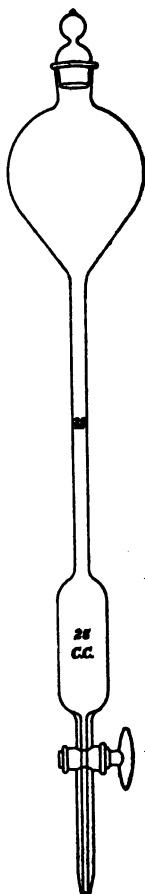
It was found that one treatment with ether was sufficient to completely remove all coloring-matter soluble therein, a second treatment with a fresh portion of ether giving no color whatever. The test is made by shaking the sample with ether, separating the ethereal from the watery layer, and comparing the color of the latter with the color of the original spirits by means of the tintometer. It is necessary, however, to bring the sample to a standard alcoholic strength, as the ether layer takes up most of the alcohol, and consequently the watery layer containing the ether-insoluble coloring-matter would be more concentrated in the case of a high proof than a low proof spirits, giving variable results. In order to insure uniformity in this respect the sample

¹ This Journal, 21, 355 (1899).

is evaporated on the water-bath until all the alcohol has been driven off; a known quantity of water-white absolute alcohol is then added, which redissolves the coloring-matter precipitated by the removal of the alcohol, making a bright solution, which is then made up to the original volume, and its color taken by means of the tintometer. A definite portion of this solution is then treated with a definite volume of ether, the watery layer separated, and its color taken by the tintometer. A comparison of the two readings will show the character of the sample, genuine spirits giving up about 40 to 50 per cent. of its color, while spirits colored by caramel alone are entirely unaffected, the ethereal layer remaining water-white.

For making the ether extraction we have found it very convenient to use a separatory funnel, which is a slight modification or rather simplification, of Bromwell's modification of Röse's apparatus for the estimation of fusel oil in spirits.¹ Our apparatus is shown in the accompanying figure, and is simply an ordinary globe-shaped separatory funnel or flask with its stem above the stop-cock expanded into a bulb holding 25 cc., the graduation coming up in the stem. The upper bulb should have a capacity of about 100 cc.

Following is the detailed method of procedure: Fifty cc. of the sample under examination are measured out at a standard (room) temperature, and evaporated on the water-bath nearly to dryness; the residue is washed into a 50 cc. glass stoppered flask, 25 cc. absolute alcohol added, and the solution, after cooling to the standard temperature, is made up to the mark with water. After mixing, 25 cc. of the solution are transferred to the separatory apparatus and treated with 50 cc. ether for half an hour, being shaken at intervals; at the end of this period, the layers having separated well, the lower layer is made up with water to the original volume, 25 cc. This is conveniently accomplished by connecting



¹ Bull. No. 49, Chem. Div., Dept. of Agriculture, p. 115.

the lower end of the apparatus with a rubber siphoning tube which carries water from an elevated flask, the inflow of water being regulated by the stop-cock of the apparatus. The contents of the flask are again shaken, and again allowed to separate (whereby the volume of the lower layer is slightly increased), and the watery layer is drawn off through the stop-cock for a reading of its color in the tintometer. At the same time a reading is taken of the 25 cc. of the solution which was not subjected to the treatment with ether; from these two readings the amount of color extracted by ether is calculated in percentages.

The accuracy of the test is much promoted by adhering carefully to the same conditions throughout, especially with regard to temperature.

Applied to a series of 34 samples of spirits known to be naturally colored, the test gave the following results:

	Color removed. Per cent.
Maximum.....	51.1
Minimum.....	36.4
Average.....	41.7

A series of 17 samples known to be artificially colored gave the following figures :

	Color removed. Per cent.
Maximum.....	23.2
Minimum.....	0.0
Average.....	14.8

The results do not show quite so wide a variation between the two sets of samples as the results obtained from the same samples by the fullers' earth test, but the ether extraction method is more satisfactory in a general way. The results obtained by the two methods were confirmatory in every case, and the former will be valuable as a supplementary test. In comparing the figures it must be kept in mind that the results by the two methods are in opposite directions; that is, fullers' earth removes the color from an artificial spirit, while ether removes the color from a natural spirit.

Since the work on this test was completed our attention was drawn to an article by Leach,¹ wherein he recommends the

¹ This Journal, 22, 207 (1900).

detection of caramel coloring in milk by means of its insolubility in ether, or rather its separation in this way from other coloring-matters (annatto and aniline orange), its identification by "any of the usual tests" to follow.

We have found the method inapplicable to vinegars colored with caramel, genuine apple vinegar giving no color when shaken with ether.

LABORATORY OFFICE OF INTERNAL REVENUE,
U. S. TREASURY DEPARTMENT, WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION
OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

A RAPID METHOD FOR THE DETECTION OF "ANILINE ORANGE" IN MILK.

BY HERMANN C. LYTHGOE.

Received October 31, 1900.

DURING the year ending September 30, 1900, there have been examined by the Department of Food and Drug Inspection of the Massachusetts State Board of Health 6137 samples of milk, of which number 45, or 0.7 per cent., contained foreign coloring-matter. Of these colored samples, 20 contained annatto, 3 contained caramel and 22, or 48 per cent., contained "aniline orange" which generic term is used to describe those azo colors used for this purpose. The statistics of the previous five years show that 0.6 per cent. of the total samples of milk were artificially colored, of which 10 per cent. contained aniline orange. The statistics of 1900 show a decided increase in the use of aniline orange as a milk "improver."

In view of the facts that if a sample is carefully colored with a view of not getting in too much, that many samples containing color are above the legal standard and that it is very difficult to tell at a casual glance whether or not a sample is colored, a rapid method for the detection of foreign coloring-matter in milk would be invaluable to the milk analyst.

In testing a sample of milk for formic aldehyde by the well-known method of boiling with an equal volume of strong hydrochloric acid containing ferric chloride,¹ the writer found upon

¹ See Twenty-ninth Annual Report of the Massachusetts State Board of Health, 1897, p. 358.

mixing the cold acid with the milk that the resulting curd was of an intense pink color. Upon further examination by the method of A. E. Leach¹ the sample was found to contain aniline orange. As a result of this, the following method is offered for the detection of aniline orange in milk.

Place about 15 cc. of milk in a porcelain casserole and add about the same quantity of hydrochloric acid (sp. gr. 1.20) gently shaking the casserole to cause thorough mixing and to break up the curd into rather coarse lumps. If the milk contains aniline orange the curd will be colored pink while if it be free from the color, the curd will be white or yellowish, according to the natural color of the milk.

If it is desired to test the milk for formic aldehyde, this same solution may be boiled after the usual addition of a drop of ferric chloride solution and if it be present the usual purple color will appear. The presence of both substances has no effect upon either test.

Commercial hydrochloric acid to which ferric chloride has been added may be used provided that the solution is not too yellow. It has been the custom in this department to add 5 cc. of a 10 per cent. solution of ferric chloride to 2 liters of commercial hydrochloric acid, and to use this solution in testing for aniline orange and formic aldehyde in milk. Sulphuric acid cannot be employed for this purpose.

This test has been in use in this department during the past year and has given satisfactory results.

It is unfortunate that this test does not detect annatto and caramel for the analyst frequently labors in vain upon suspicious looking samples, but by applying this simple method, all the samples colored with aniline orange will be pointed out at the same time that the analyst makes the test for formic aldehyde, without the loss of time, reagent, or sample.

¹ A. E. Leach : This Journal, 20, 207 (1900).

NOTE.

Preparation of Triphenylchlormethane.—In my paper on "The Preparation of Triphenylchlormethane," in the November number, page 752, this Journal, a misstatement occurs which gives an ambiguous meaning to the paper. The first paragraph should read: "It is generally stated * * * *triphenylmethane* is the principal product of the reaction," and not *triphenylchlormethane*, as it reads now.

I also wish to take this opportunity to state that Thorp ("Inorganic Chemical Preparations," p. 39) recommends the preparation of aluminum chloride, in small quantities, by the same method as given in my paper.

M. GOMBERG.

NEW BOOKS.

DIE AETHERISCHEN ÖLE. Von E. GILDEMEISTER und FR. HOFFMANN, bearbeiten im auftrage der firma Schimmel & Co. in Leipzig. Berlin: verlag von Julius Springer. 1899.

THE VOLATILE OILS. By E. GILDEMEISTER and FR. HOFFMANN. Written under the auspices of the firm of Schimmel & Co., Leipzig. Authorized translation by EDWARD KREMERS, Madison, Wis. Milwaukee: Pharmaceutical Review Publishing Co. 1900.

THE CHEMISTRY OF ESSENTIAL OILS AND ARTIFICIAL PERFUMES. By ERNEST J. PARRY, B.Sc., etc. London: Scott, Greenwood & Co. 1899. New York: D. Van Nostrand Company.

The subject of the essential or volatile oils has until very recently been given a distinctly secondary place in the chemical text-books in comparison with the class of fixed oils. Indeed, a few lines about terpenes and camphors has been thought quite a sufficient treatment by the writers of some of the most reputable text-books until quite lately. But this state of things could not remain in view of the brilliant work done in recent years in this branch by men like Wallach, Tiemann, and von Baeyer. As Prof. Emil Fischer, of Berlin, has recently remarked, it is a chapter of organic chemistry that has undergone more rapid development within the past fifteen years than any other.

It is fortunate that, the need having been felt, it should have been filled by the firm of Schimmel & Co., of Leipzig, who are so intimately and honorably connected with the industry of the

essential oils, stepping forward and commissioning scholarly and competent men like Drs. Gildemeister and Hoffmann to write a book covering this ground. The result is the magnificent volume before us in which, as Prof. Kremers says, we find a happy blending of history with chemical science and technology that is quite unique in modern chemical literature.

With true German thoroughness, the work begins with an Historical Introduction, in which we have an account of the spice trade in antiquity and during the middle ages, illustrated by two colored charts, showing "the highways of commerce" in ancient times and in the middle ages, respectively.

This introduction also contains a history of volatile oils, and a history of the methods of distillation and of distilling apparatus. This portion of the work shows much antiquarian knowledge and research and is from the pen of Dr. Fr. Hoffmann, the former editor of the "Pharmaceutische Rundschau," of New York, now resident in Berlin. It is copiously provided with bibliographic references and is of very great interest to the historical student.

The General Part which follows, discusses first the theoretical basis for obtaining volatile oils by steam distillation and then takes up for enumeration and scientific description the more commonly occurring constituents of volatile oils. This descriptive part is very valuable to the chemist, as it epitomizes the latest and most accurate results in this group, and gives full references to the journal literature in foot-notes. This is followed by an account of the methods of examination of volatile oils, both physical and chemical, and lastly we have a list of plants arranged according to families, from which volatile oils are obtained.

The third and longest division of the book is the Special Part, in which we have the history, origin, preparation, properties, composition, examination, and commercial statistics of the volatile oils. The number of individual oils so treated in detail in the original German work is 422, and in Prof. Kremers' translation 430.

Besides the two colored charts already referred to as found in the Historical Introduction, we have two colored maps of Ceylon and of Calabria and Sicily, respectively, and numerous wood-

cuts illustrating the conditions of production of some of the essential oils.

The German publication forms a stately volume of 919 pages, bound in half morocco, and will form a most satisfactory addition to any chemical library.

A few words specially with regard to the American edition. In Prof. Kremers, of the University of Wisconsin, the authors found a most competent translator and editor for the English issue, as it is a field in which he has himself made valuable contributions and with which he is entirely familiar. By condensing several of the sections in the Historical Introduction and putting the bibliographical notes together at the end of the book he has been able to bring all the matter in the compass of 733 pages, without sacrifice of any important feature.

The charts and illustrations are all reproduced and the book is well printed and finely bound.

The work of Mr. Parry on "The Chemistry of Essential Oils and Artificial Perfumes," which also appeared in 1899, while not so ambitious a work as that of Drs. Gildemeister and Hoffmann is, nevertheless, a valuable work, written throughout in a scientific spirit and with a careful consideration of available sources of information. Without attempting anything in the way of a history of the subject, it starts in with the general properties of the essential oils briefly stated, and then gives an excellent review of the compounds occurring in essential oils, stating the most approved views with the aid of structural formulas. The sections on the preparation and analysis of the essential oils are relatively brief and deal with the subject only in a general way. The systematic study of the oils, which takes up the body of the book, deals with them according to the botanical relationship of the plants yielding them, that is, according to natural orders. This part seems to have been well done and the journal literature is considered throughout. A chapter on terpeness oils follows. The chemistry of artificial perfumes, to which 41 pages are devoted, is well treated, in fact is the best summary of our knowledge which, as far as the writer knows, has appeared in the English language. It makes frequent reference to the patent literature, giving numbers and dates of patents, giving an account of the ionone and violet-oil patent litigation, quoting Tiemann's

and Fritsche & Co.'s patents in full, explains the methods for the manufacture of vanillin, heliotropin, artificial musk, hyacinth, etc. The appendix contains a valuable table of the constants for the more important essential oils. The book can be thoroughly commended as furnishing a compact and convenient reference book on the subject. SAMUEL P. SADTLER.

CHEMISCH-TECHNISCHE UNTERSUCHUNGSMETHODEN. Herausgegeben von DR. GEORG LUNGE. Dritter Band, mit 104 abbildungen. Vierte auflage. xxii + 1082 pp. Berlin: Verlag von Julius Springer. 1900. Price, M. 23.

This volume contains Mineral Oils and Examination of Lubricants, by Dr. D. Holde; Oils and Fats and Special Methods of the Oil and Fat Industry, by Dr. Rob. Henriques; Examination of Resins, Balsams and Gum Resins, and Drugs and Galenical Preparations, by Dr. Karl Dieterich; Caoutchouc and Caoutchouc Wares, by Dr. Rob. Henriques; Ethereal Oils, by Dr. E. Gildemeister; Raw Materials, Products, and By-products of Sugar Manufacture, by Dr. O. von Lippmann and Dr. Georg Pulvermacher; Starch, by Dr. C. von Eckenbrecher; Spirits, by Dr. A. Ebertz; Brandy and Liqueurs and Vinegar, by Dr. G. Schüle; Examination of Wine, by Dr. Karl Windisch; Beer, by Prof. L. Aubry; Examination of Vegetable Material Containing Tannin, by Dr. C. Counciler; Leather, by Dr. Joh. Paessler; Paper, by W. Herzberg; Ink, by O. Schluttig and Dr. G. S. Newmann; Organic Preparations, by Dr. J. Messner; The Tartaric Acid Industry and Citric Acid Manufacture, by Dr. Hermann Rasch; and Organic Dyes and the Examination of Textile Fibers and Loading Materials, by Dr. R. Gnëhm.

This is a wide range of subjects, which seem in the main to be well covered. The authors confine themselves very closely to methods of testing. Very little is said about methods of manufacture. This seems on the whole something of a defect, for while it is true that information of this sort is otherwise attainable, it is widely scattered and one of the chief values of such a compilation as this is found in the saving of the time of the busy working chemist. Very few chemists can expect to fully cover, even in analytical knowledge, so wide a range as is here presented.

The "Anhang" contains numerous tables from the body of the work printed on one side of the paper for pasting on the

laboratory wall. Some of these tables are: Correction of the Specific Gravity of Petroleum for Different Temperatures; Specific Gravity of Aqueous Glycerine Solutions; Refractive Index of Aqueous Glycerine Solutions; Specific Gravity of Methyl Alcohol; Specific Gravity of Mixtures of Ortho- and Paratoluidin; Determination of Monoethyl and Diethyl Anilin; Solidifying Points of Acetic Acid; Specific Gravity of Oxalic Acid Solutions.

The book is a monument of patient industry and is worth more than it costs. It is a good piece of book work mechanically considered.

E. H.

BOOKS RECEIVED.

Bulletin of the United States Geological Survey, No. 176. Some Principles and Methods of Rock Analysis. 114 pp.

The Hessian Fly in West Virginia and How to Prevent Losses from its Ravages. By A. D. Hopkins, Ph.D. Bulletin 67. W. Va. Agricultural Experiment Station, Morgantown, W. Va. August, 1900. 16 pp.

Report on the Geology of the Essequibo, Potaro, Konawaruk and Demerara Rivers, British Guiana. Georgetown, Demerara. 1900. 82 pp. 4to.

Quantitative Chemical Analysis, adapted for use in the Laboratories of Colleges and Schools. By Frank Clowes, D.Sc. (Lond.), and J. Bernard Coleman, A. R. C. Sc. (Dublin). Fifth Edition. Philadelphia: P. Blakiston's Son & Co. 1900. xxiv + 592 pp. Price \$3.50.

Decision of the U. S. Circuit Court of Appeals on the Indoine Blue Case. 27 pp. Kuttroff, Pickhardt & Co., P. O. Box 2885, New York City.

Chemisch-technische Untersuchungsmethoden. Herausgegeben von Dr. Georg Lunge. Dritter Band, mit 104 in den Text gedruckten Abbildungen. Vierte vollständig umgearbeitete und vermehrte Auflage. Berlin: Verlag von Julius Springer. 1900. xxii + 1082 pp. Anhang iv + 55. Price, 23 marks.

Victor Von Richter's Textbook of Inorganic Chemistry, edited by Prof. H. Klinger, University of Königsberg. Authorized Translation by Edgar F. Smith, Professor of Chemistry in the University of Pennsylvania. Assisted by Walter T. Taggart, Instructor in Chemistry. Fifth American from the Tenth German Edition, carefully revised and corrected. With 68 illustrations in wood and colored lithographic plate of spectra. Philadelphia: P. Blakiston's Son & Co. 1900. xii + 430 pp. Price, \$1.75.

An Investigation into the Causes of So-called Uric-acid Lesions,

and a Rational Therapeusis of the Uratic Diathesis. By Alfred Careno Croftan, A.M., M.D., Pasadena, Cal. Reprinted from the New York Medical Journal, for September 22, 1900. 22 pp.

The Economic Entomology of the Sugar Beet. Bulletin No. 60. Agricultural Experiment Station, Urbana, Ill. August, 1900. 136 pp.

Commercial Organic Analysis. A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the Various Organic Chemicals and Products Employed in the Arts, Manufactures, Medicines, etc., with Concise Methods for the Detection and Determination of Their Impurities, Adulterations, and Products of Decomposition. By Alfred H. Allen, F.I.C., F.C.S. Third Edition, rewritten and enlarged. Vol. III, Part I. Tannins, Dyes and Coloring-matters, Writing Inks. Revised and edited by J. Merritt Mathews, Ph.D. Philadelphia: P. Blakiston's Son & Co. 1900. 589 pp. Price, \$4.50.

A Text-book of Important Minerals and Rocks, with Tables for the Determination of Minerals. By S. E. Tillman. New York: John Wiley & Sons. 1900. ix + 176 pp. Price, \$2.00.

A Handbook of Industrial Organic Chemistry Adapted for the Use of Manufacturers, Chemists, and all Interested in the Utilization of Organic Materials in the Industrial Arts. By Samuel P. Sadtler, Ph.D., F.C.S. Third Revised and Enlarged Edition. Philadelphia: J. B. Lippincott & Co. 1900. Price, \$5.00.

Chemical Technology or Chemistry in its Applications to Arts and Manufactures. Edited by Charles Edward Groves, F.R.S., and William Thorp, B.Sc., with which is Incorporated Richardson and Watts' Chemical Technology. Vol. III.—Gas Lighting. By Charles Hunt. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1900. Price, \$3.50.

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COUNCIL.

The following resolution was approved by Council, June 15, 1900:

"Resolved, That the President of the American Chemical Society is hereby authorized and directed to appoint a committee, of which he himself shall be Chairman, with power to confer and to make arrangements with Section C, with any officers or committees of the American Association for the Advancement of Science, and with other organizations affiliated with the American Association for the Advancement of Science, for future summer meetings of the American Chemical Society and Section C."

NAMES PROPOSED FOR MEMBERSHIP.

Bolling, Randolph, Va. I. C. & C. Co., Radford Blast Furnace, Radford, Va.

Brown, Walter B., care Nelson Morris & Co., U. S. Yards, Chicago, Ill.

Cabot, Samuel, 70 Kilby St., Boston, Mass.

Diehl, Oscar C., care Parke, Davis & Co., Detroit, Mich.

Hall, Everett J., Passaic, N. J.

Hillyer, Homer W., Madison, Wis.

Kniffen, Frederick, Indian Head, Md.

Lucas, Alfred, Survey Dept., Public Works Ministry, Cairo, Egypt.

Lyons, Philip D., Md. Steel Co., Sparrows Point, Md.

Nathan, Albert F., 603 Mumford Court, Kansas City, Mo.

Reid, E. Emmet, College of Charleston, Charleston, S. C.

Root, W. W., 186 Eugenie St., Chicago, Ill.

Sears, Frederick E., St. Paul's School, Concord, N. H.

Seward, George O., Holcomb Rock, Va.

Walker, Claude F., Calumet, Mich.
 Wiley, Walter B., Bramwell, W. Va.
 Willcox, Frank A., Oakland, Bergen Co., N. J.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Calvert, Joseph E., Etna, Allegheny Co., Pa.
 Condit, Louis C., 139 Lafayette Ave., Brooklyn, N. Y.
 Kohnstamm, Lothair S., 133 E. 71st St., New York City.
 Thomas, T. Lewis, 71 Broadway, New York City.
 Warren, Robert, S. 6th St., Terre Haute, Ind.

CHANGES OF ADDRESS.

Archibald, Eben H., Harmony, Colchester Co., Nova Scotia.
 Arnold, Fred. N., care The N. K. Fairbank Co., St. Louis, Mo.
 Arnott, G. W. Campbell, 26 Broadway, New York City.
 Beach, W. M., 954 W. North Ave., Allegheny, Pa.
 Behr, Gustave E., Jr., Harvard Univ., Cambridge, Mass.
 Bevier, Miss Isabel, Univ. of Ill., Champaign, Ill.
 Browne, Charles A., Jr., Univ. of Goettingen, Goettingen, Germany.
 Burk, W. E., Male High School, Louisville, Ky.
 Burn, Harry, care Sloss-Sheffield S. & I. Co., Birmingham, Ala.
 Campbell, Archibald, 3140 Duwell Ave., Walnut Hills, Cincinnati, Ohio.
 Campbell, George F., 82 Broadway, New Haven, Conn.
 Cayvan, L. L., 499 Adams St., Chicago, Ill.
 Coutie, William, 2129 7th Ave., Troy, N. Y.
 Craig, A. G., 6112 Station St., Pittsburg, Pa.
 Davis, Charles B., care Dr. Wyatt, 39 S. William St., New York City.
 Davison, John M., 340 Oxford St., Rochester, N. Y.
 Dorr, John V. N., Golden Gate M. & M. Co., Deadwood, S. D.
 Downey, James E., High School, Holyoke, Mass.
 Dustin, Guy K., 30 Lenango St., Binghamton, N. Y.
 Ellis, Carleton, 195 Winchester St., Keene, N. H.
 Ellis, Geo. H., 163 Randolph St., Chicago, Ill.
 Fischer, Robert, 810 Franklin Ave., Columbus, O.
 Gallivan, F. B., 56 Prospect Place, Brooklyn, N. Y.
 Garrigues, W. E., 1123 Broadway, New York City.
 Given, Arthur, 1 Plymton St., Worcester, Mass.
 Hall, Robert W., University Heights, Bronx, N. Y. City.
 Hamilton, Louis P., 222 E. Beaux St., Washington, Pa.
 Hodges, G. C., Box 88, New Hartford, N. Y.

Horsford, Roger F., care Am. Bell Telephone Co., 125 Milk St.
Boston, Mass

Isaacs, A. S., 1214 Sheffield St., Allegheny, Pa.

Keller, A. C., Apartado A., Aguascalientes, Mexico.

Kittredge, Harvey G., The Kay and Ess. Co., Dayton, O.

Krug, W. H., Div. of Chem., U. S. Dept. of Agr., Washington,
D. C.

Levine, Edmund J., 337 W. 88th St., New York City.

Lippincott, Warren B., Am. S. & R. Co., Argentine, Kas.

Lythgoe, H. C., Room 501, State House, Boston, Mass.

Mabery, C. F., North Gorham, Me.

Mathewson, E. P., Establacimiente del Playa Blanca, Antofogasta, Chili, S. C.

Mixer, C. T., Joplin, Mo.

Murrill, Paul, Hickory, N. C.

Parker, T. J., care General Chem. Co., 32 Liberty St., New
York City.

Parmelee, H. C., 1733 High St., Denver Colo.

Porter John J., Observatory Ave., Hyde Park, Cleveland, O.

Redding, Allen C., Golconda Mine, Sumpter, Ore.

Reese, H. J., Livingston, Mont.

Richardson, Clifford, Director N. Y. Testing Lab., Long Is-
land City, N. Y.

Rickards, Burt R., 162 Salem St., Malden, Mass.

Ritchey, Joseph C., Nat. Steel Co., Mingo Junction, O.

Rosell, Claude A. O., 268 W. Broadway, New York City.

Sanborn, E. R., care Alice Furnace, Sharpsville, Pa.

Smith, A. L., 653 Union Ave., Englewood, Ill.

Soper, G. A., 29 Broadway, New York City.

Sticht, Gustave A. H., care Tartar Chem. Co., Jersey City,
N. J.

Stone, Geo. C., 115 Broadway, New York City.

Syme, Wm. A., cor. North and Person Sts., Raleigh, N. C.

Thomas, N. Wiley, Rooms 330-332, City Hall, Philadelphia,
Pa.

Torrey, Henry A., 75 S. Prospect St., Burlington, Vt.

Touceda, Enrique, Room 44, 51 State St., Albany, N. Y.

Wilder, S. W., Jr., 77 Broad St., Boston, Mass.

Worstall, R. A., 1246 E. Madison Ave., Cleveland, O.

ADDRESS WANTED.

Stursberg, J. A., formerly of 18 E. 67th St., N. Y. City.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The regular meeting was held May 10th.

Mr. Edwin A. Hill presented a paper entitled "On a System of Chemical Indexing Adopted by the Classification Division of the U. S. Patent Office."

WILLIAM H. KRUG, *Secretary.*

Proceedings.

TWENTY-FIRST GENERAL MEETING.

The Twenty-first General Meeting of the American Chemical Society was called to order at 12.35 P.M., Monday, June 25, 1900, in Room 309, Havemeyer Hall, Columbia University, New York City.

The president introduced Dr. Charles F. McKenna, chairman of the New York Section, who addressed a few words of welcome to the visiting chemists.

Responses were made by Prof. Jas. Lewis Howe, on behalf of Section C of the American Association for the Advancement of Science, and Dr. Wm. McMurtrie, on behalf of the American Chemical Society.

After a few announcements, the meeting was adjourned till 2 P.M.

Afternoon Session.—At 2 P.M. the Society was called to order again and the minutes of the last general meeting as already printed in the Journal were approved.

A paper on "The Composition of Abietic Acid" was read in abstract by the author, Hermann A. Loos.

Mr. Marston Taylor Bogert read a paper on "Experiments with Some Substituted Benzoic Acids and their Nitriles," prepared by himself and August H. Gotthelf. This was followed by two other papers by the same authors, the titles of the papers being "The Direct Synthesis of Ketodihydroquinazolines from Orthoamido Nitriles" and "The Direct Synthesis of Ketodihydroquinazolines from Orthoamido Acids."

A paper "On Some Derivatives of Phenyl Ether," by H. W.

Hillyer, was read by the author, after which the session adjourned.

A meeting of the Council of the Society was held in Room 311, Havemeyer Hall, at 4.15 P.M. At 8 P.M. the chemists enjoyed a "Smoker" at the Chemists' Club, 108 W. 55th St., given by the New York Section of the Society.

TUESDAY, JUNE 26, 1900.

Forenoon Session.—The morning session was called to order at 10.40 A.M. in the Assembly Hall of the Chemists' Club. Mr. T. J. Parker, vice-president of the Club, was introduced by the president, and welcomed the chemists in a few words.

A paper on "The Metric System, Past, Present, and Prospective," was presented by Rufus P. Williams, and discussed by Messrs. Parker, Seaman, and Hillebrand, the last of whom offered the following resolution :

Resolved, That this Society is strongly in favor of the passage of H. R. Bill 104, looking to the adoption and use of the Metric System, and that the secretary be instructed to so inform the Chairman of the Committee on Coinage, Weights, and Measures of the House of Representatives in Washington.

This was referred without debate to the Council for consideration and report at the December meeting as to the advisability of the Society adopting it.

A paper on "The Reduction Products of Dehydromucic Acid" was read by A. S. Wheeler and discussed by W. A. Noyes. The following papers were then presented by their authors :

"The Detection of Coal-tar Dyes in Food Products," by A. L. Winton.

"Estimation of Fat in Sweetened Condensed Milk," by Joseph F. Geisler.

"Some Analyses of Milk and Cream, with Reference to the Condition of Fat Globules," by H. C. Sherman.

"The Action of Various Preservatives upon Cider," by E. H. S. Bailey.

"The Determination of the Formulas of the Hydrocarbons and Chlorine Derivatives in Pennsylvania, California, Japanese

and Canadian Petroleum by Molecular Refraction," by Charles F. Mabery and O. J. Sieplein.

"The Sulphur Compounds and their Oxidation Products and the Unsaturated Hydrocarbons in Canadian Petroleum," by Charles F. Mabery and W. O. Quayle.

"Composition of the Hydrocarbons in Pennsylvania Petroleum, Liquids and Solids above 216°," by Charles F. Mabery.

"Composition of the Hydrocarbons in California Petroleum, Liquids and Solids," by Charles F. Mabery.

"Composition of the Nitrogen Compounds in California Petroleum," by Charles F. Mabery.

"The Chlorine Derivatives of the Hydrocarbons in California Petroleum," by Charles F. Mabery and O. J. Sieplein.

The meeting was then adjourned till 2.30 P.M.

Afternoon Session.—The afternoon session was called to order at 2.30 P.M. at the Chemists' Club.

The secretary called attention to the death of Mrs. Rachel Lloyd, a former member of the Society, and moved that Dr. C. F. Mabery be requested to prepare a suitable memorial to be printed in the Journal. The motion was passed unanimously.

The committee appointed to prepare a memorial on the late Professor Bunsen presented its report by title. The report was referred to the Committee on Papers and Publications.

After some announcements the following papers were read :

"Experimental Demonstration of the Manufacture of Sulphuric Acid". (by the Contact Process), by Charles L. Reese and G. C. Stone.

"Production of Caustic Soda and Bleaching-powder by Electrolysis," by Hugh K. Moore.

"The Incubator Test for Determining the Purity of Sewage Effluents," by Leonard P. Kinnicutt.

"Bacterial Action in the Purification of Sewage by Chemicals," by Leonard P. Kinnicutt.

"An Experimental Study of the Gas-producing Power of *Bacillus Coli Communis* under Different Conditions of Environment," by Mary Engle Pennington and G. C. Küsel. This paper was read by Dr. Pennington and discussed by Messrs. Harper and Doremus.

The secretary moved that Professor Edward W. Morley, of Cleveland, Ohio, and Professor Wilhelm Ostwald, of Leipzig, Germany, be elected honorary members of the Society. The motion was adopted unanimously.

After the reading of a "Note on the Landsberger-McCoy Apparatus," by W. D. Bancroft, and a paper on "The Action of Potassium Hydroxide on Chloroform," by A. P. Saunders, read by Prof. Bancroft, and some announcements, the Twenty-first General Meeting of the Society was adjourned *sine die*.

WEDNESDAY.

At 7 P.M. on Wednesday, June 27, the chemists enjoyed a dinner at Hotel Majestic. On account of the unpromising weather the dinner was in the dining hall of the hotel, instead of being upon the roof garden as had been contemplated.

Dr. Charles F. McKenna presided and acted as toast-master.

Toasts were responded to by President William McMurtrie, Prof. L. O. Howard, permanent secretary of the A.A.A.S., Prof. Jas. Lewis Howe, vice-president A. A. A. S., Section C, Dr. Mary Engle Pennington, Prof. Elihu Thomson, Dr. Charles Baskerville, Prof. B. W. Kilgore, and Dr. L. P. Kinnicutt.

ALBERT C. HALE, *Secretary*.

BOARD OF DIRECTORS.

The Board of Directors of the American Chemical Society met at the Chemists' Club, New York City, at 9.45 P.M., June 25, 1900. There were present Messrs. McMurtrie, Hale, Hallock, Doremus, and Smith.

The sum of fifty dollars, or so much thereof as may be necessary, was appropriated from funds of the Society not otherwise appropriated for the purpose of preparing a card catalogue for the library.

The librarian was authorized to expend a sum not exceeding twenty-five dollars for new shelving for the library.

The sum of fifteen dollars and fifty-five cents was appropriated to reimburse the expenses of the president in going to Washington to appear before the Committee of Congress upon the question of establishing a National Standards Bureau.

The president of the Society was authorized to take from the library temporarily such material as he may wish to use in preparing a review of the progress of industrial chemistry.

It was ordered that the insurance on the library be kept sufficient to cover the current stock of Journals on hand from time to time.

The Board then adjourned.

ALBERT C. HALE, *Secretary*.

COUNCIL.

A meeting of the Council of the American Chemical Society was held in Room 311, Havemeyer Hall, Columbia University, New York City, at 4.15 P.M., Monday, June 25, 1900.

There were present Messrs. McMurtrie, Catlin, Doremus, Hale, Hallock, Hart, Hillebrand, Kinnicutt, Long, Mabery, Mathews, McPherson, Munroe, A. A. Noyes, W. A. Noyes, E. E. Smith, and Venable.

The minutes of the December meeting, as already printed in the Journal, were approved.

The president gave a brief review of the present condition and needs of the Society, after which the following resolution was adopted :

Resolved, That Sections (1) and (2) of the Finance Committee's report as adopted at the last general meeting of the Society be amended to read as follows :

- (1) Before December 15 of each year, each officer of the Society shall submit to the president a schedule comprising the estimated expenses of his office, in detail, for the ensuing year. The president shall, in advance of the annual meeting, submit these estimates to a Committee on Estimates, consisting of the Finance Committee, the president, the secretary, and the treasurer, who shall consider them in the relation to the probable income of the Society for the ensuing year, and report the result of their deliberations, together with the original estimates, with recommendations of appropriations to the Council at the annual meeting.
- (2) After such report shall have been submitted, the Council shall recommend such appropriations for

each office as may be deemed advisable, and the Directors shall, upon such recommendation from the Council, make necessary appropriations in accordance therewith.

After some discussion regarding the question of apportionment of the funds of the Society for the benefit of Local Sections, the following motion, presented by W. A. Noyes, was adopted :

Resolved, That the Council recommends that the Local Sections be requested to keep their expenses as low as they deem consistent with the best interests of the Society in their locality ; also that they be requested not to draw funds from the treasury except as required for the payment of bills.

On motion of Dr. Mabery, this motion was reconsidered, and, after some discussion, again passed by the Council.

The following resolutions were also passed :

Resolved, That the president of the Society be authorized and directed to appoint a committee, of which he himself shall be chairman, with power to arrange for the celebration of the twenty-fifth anniversary of the foundation of the Society, which will occur on April 6, 1901, in conformity with the action taken by the Council upon that subject at the last general meeting of the Society.

Resolved, That the president of the Society appoint a committee of five, of which he himself shall be one, with power to make a new contract for the printing of the Journal of the Society.

The following named gentlemen were appointed to constitute the Committee on Contract : Messrs. McMurtrie, C. B. Dudley, M. L. Griffin, A. D. Little, and H. N. Stokes.

The following communication from the librarian was read by the secretary and ordered to be included in the minutes of the Council, and printed in the Journal :

NEW YORK, June 23, 1900.

Dr. Wm. McMurtrie, President American Chemical Society :

DEAR SIR : I submit the following statement in response to a resolution of the Board of Directors of the Society "that the librarian be requested to furnish to the Board of Directors a survey of the sets of the Journal now the property of the Society that the same may be scheduled for use."

There have been 10 issues of the Proceedings and 216 issues of the Journal.

There are at present in the custody of the librarian 3,672 copies of the Proceedings, and 44,756 copies of the Journal, or a total of 48,428 copies. These are stored as follows :

Proceedings in Garfield Storage	3,213	
" at Chemists' Club.....	459	3,672
Journals in Garfield Storage	33,257	
" at Chemists' Club	11,499	44,756
Total Proceedings and Journals...		48,428

These figures so far as they refer to the material in the Garfield Storage Warehouse are based on an inventory furnished me by a former librarian.

Of the Proceedings, No. 5 of Vol. II is out of print, but of the other issues the number of copies ranges from 100 in the case of Vol. I, No. 1, to 672 in that of Vol. II, No. 2.

The issues of the Journal of which we have less than 50 copies each are as follows :

	Copies.
Vol. III, single number 1-6.....	38
" " number 7.....	35
" " single number 8-12	25
" IV, number 12	48
" V, single number 2-3.....	48
" VI, " " 1-2.....	26
" " number 3.....	18
" " " 4	30
" XVII, number 10	34
" XVIII, " 6	43
" XX, " 3	42

Or there are 11 issues of which we have less than 50 copies each. In addition to these there are :

31 issues of which we have from	50 to 100 copies each.
132 " " " " " " " " " "	100 to 250 " "
24 " " " " " " " " " "	250 to 500 " "
18 " " " " " " " " " "	over 500 copies each.

It appears, therefore, that at the present time we can not furnish a set of the Proceedings, and can furnish only eighteen sets

of the Journal. In view of this fact, I would suggest that at least ten sets of the Journal be reserved to be sold only in sets.

It will be noticed from the foregoing statement that nearly one-fourth of our entire stock of Proceedings and Journals is stored at the Chemists' Club in 55th St. The library is covered by insurance, but so far as I know the stock of Journals is not. I would suggest that a special policy be taken out, the amount of which shall be increased monthly or bimonthly by a sum sufficient to cover the issues received in the meantime, less those disposed of.

The stock of Journals stored at the Chemists' Club is deposited in a room which the librarians of the Society have simply appropriated without any action on the part of the Trustees of the club granting the use of such room. The club may at any time require this space, in which event it would be necessary for the librarian to find other storage for these Journals. I would therefore recommend that the Council be requested to take such action as may be necessary either to rent from the club the room at present used by the Society, or to procure storage elsewhere. The space available in this room will probably answer our requirements for two or three years, at the end of which time our supply of certain issues will doubtless be so much reduced as to make it necessary for the Society to determine whether the present policy of carrying a stock of each issue, with the necessity of reissuing certain numbers from time to time, be continued, or whether it may not be advisable to abandon the present plan, and to supply the Journals only so long as the first issue lasts.

Yours truly,

E. G. LOVE, *Librarian*.

It was ordered that the eighteen sets of the Journal now available be reserved to sell intact as sets.

The matter of the storage of the numbers of the Journal was referred to the committee authorized to make a new contract for printing the Journal.

The following motions with reference to the library were adopted :

Resolved, That a card catalogue of the library be prepared

under the direction of the librarian as soon as the work can be conveniently accomplished, and that the Directors be requested to appropriate for such purpose the sum of fifty dollars, or so much thereof as may be necessary, from funds of the Society not otherwise appropriated.

Resolved, That the Directors be requested to appropriate a sum not exceeding twenty-five dollars to furnish new shelving for the library.

Resolved, That a committee, consisting of the librarian and two other members of the Society, be appointed with power to eliminate useless matter from the library.

Upon motion of Dr. Hart, the Committee on Abstracts was discharged. The following resolution was then presented and adopted :

Resolved, That a committee of five be appointed by the chair to report at the annual meeting upon the advisability of preparing a title index of papers for the Journal.

The following motion was adopted .

Moved, That all nominees to membership up to the close of this meeting be considered as acted upon by the Council, and the secretary shall declare them elected whenever all the other requirements of the constitution in regard to them as nominees shall have been met.

A communication from Mr. Ewell, chairman of the Committee on Standards for Instruments of Measure, was presented, showing briefly what that committee has already accomplished.

Prof. John H. Long presented a communication from the Chicago Local Section inviting the Society to hold its winter meeting in Chicago. He most heartily urged the acceptance of the invitation which was renewed this year, and showed that while Chicago acquiesced last year in the decision that it was best for the Society to hold its winter meeting then in New Haven, yet this year he hoped that nothing would prevent the acceptance of the invitation, which was cordially renewed for the winter of 1900.

Upon motion, it was resolved that the cordial invitation extended by the Chicago Section to hold the next general meeting in the city of Chicago be and the same is hereby accepted with much pleasure. It was also resolved that the meeting be held

during the last week in December, and that the exact date for the meeting be fixed by the president and secretary.

After some discussion regarding qualifications for membership, it was voted that the Committee on Membership be requested to adopt a more liberal interpretation of that portion of the constitution which treats of this subject.

After some discussion of some other matters, upon which no action was taken, the Council adjourned.

ALBERT C. HALE, *Secretary*.

COMMITTEE ON TWENTY-FIFTH ANNIVERSARY.

Wm. McMurtrie, *Chairman*.

Albert C. Hale, *Secretary*.

H. C. Bolton,	A. A. Noyes,
C. L. Jackson,	C. E. Munroe,
J. H. Long,	C. F. Chandler,
Charles Baskerville,	S. W. Johnson,
W. L. Dudley,	A. B. Prescott,
H. H. Nicholson,	Ira Remsen,
W. B. Rising,	E. W. Morley,
W. P. Mason,	C. B. Dudley,
G. F. Barker,	C. A. Goessmann,
J. W. Mallet,	Henry Morton,
Jas. Lewis Howe,	C. A. Doremus,
J. H. Appleton.	

COMMITTEE TO ELIMINATE USELESS MATTER FROM LIBRARY.

E. G. Love,	E. E. Smith,
A. P. Hallock.	

COMMITTEE ON TITLE INDEX.

Wm. McMurtrie,	A. A. Noyes,
W. A. Noyes,	C. F. Mabery,
C. E. Munroe.	

NAMES PROPOSED FOR MEMBERSHIP.

Clark, Alfred N., Agricultural College, Mich.
 Harrington, Charles, Harvard Med. School, Boston, Mass.
 Harris, Isaac F., Chapel Hill, N. C.
 Jürgensen, Dr. Rolof, care of Dr. Jürgensen and Bauschlicher,
 Techn.-Bureau für die Chem.-Industrie, Prag-Zizkov, Austria.

Shepard, C. H., Pinole, Contra Costa Co., Cal.
Smith, Lyman G., Roxbury High School, Warren St., Boston, Mass.
Smith, Thorn, Isabella, Polk Co., Tenn.
Wainwright, John W., 177 W. 83rd St., N. Y. City.
Young, Clare C., 518 Alvarado, Los Angeles, Cal.

NAME PROPOSED FOR ASSOCIATE MEMBERSHIP.

Medcalf, George T., Box 280, Eureka, Humboldt Co., Cal.

NEW MEMBERS ELECTED JUNE 26, 1900.

Allen, Richard F., Hart Park, West New Brighton, S. I., N. Y.
Hancock, Wm. J., Erasmus Hall High School, Brooklyn, N. Y.
Logan, Lily, Howardsville, Va.
Norton, (Mrs.) Alice P., 47 Hancock St., Auburndale, Mass.
Richards, Alfred N., 437 W. 59th St., N. Y. City.
Sundstrom, Carl, Solvay Process Co., Detroit, Mich.
Sundstrom, Karl J., Trenton, Mich.
Taylor, Thomas M., Oberlin, O.
Torrey, Joseph, Jr., 8 Avon St., Cambridge, Mass.
Waddell, John, School of Mining, Kingston, Ontario.

ASSOCIATES ELECTED JUNE 26, 1900.

Pretzfeld, Chas. J., 1211 Madison Ave., N. Y. City.

NEW MEMBERS ELECTED JULY 20.

Bolling, Randolph, V. I. C. & C. Co., Radford Blast Furnace, Radford, Va.
Brown, Walter B., Nelson Morris & Co., U. S. Yards, Chicago, Ill.
Diehl, Oscar C., Parke, Davis & Co., Detroit, Mich.
Hall, Everett, J., Passaic, N. J.
Hillyer, Homer W., Madison, Wis.
Kniffen, Frederick, Indian Head, Ind.
Lucas, Alfred, Survey Dept., Public Works Ministry, Cairo, Egypt.
Lyons, Philip D., Md. Steel Co., Sparrows Point, Md.
Nathan, Albert F., 603 Mumford Court, Kansas City, Mo.
Reid, E. Emmet, College of Charleston, Charleston, S. C.
Root, W. W., 186 Eugenie St., Chicago, Ill.
Sears, Frederick S., St. Paul's School, Concord, N. H.
Seward, George O., Holcomb Rock, Va.

Walker, Claude F., Calumet, Mich.
Wiley, Walter B., Bramwell, W. Va.
Willcox, Frank A., Oakland, Bergen Co., N. J.

ASSOCIATES ELECTED JULY 20, 1900.

Calvert, Joseph E., Etna, Allegheny Co., Pa.
Condit, Louis C., 139 Lafayette Ave., Brooklyn, N. Y.
Kohnstamm, Lothair S., 133 E. 71st St., N. Y. City.
Thomas, T. Lewis, 71 Broadway, N. Y. City.
Warren, Robert, S. 6th St., Terre Haute, Ind.

CHANGES OF ADDRESS.

Archibald, E. H., Harmony, Colchester Co., Nova Scotia.
Enright, Bernard, 330 E. 4th St., So. Bethlehem, Pa.
Johnson, Treat B., Westville, Conn.
Langmuir, A. C., care of Mark & Rawolle, 9 Van Brunt St.,
Brooklyn, N. Y.
Lipman, J. G., Woodbine, N. J.
Quinan, W. R., Guardian Bldg, Cape Town, So. Africa.
Rising, H. R., 39 S. 10th St., Newark, N. J.
Rolfe, Geo. W., 1 Cleveland St., Cambridge, Mass.
Scherr, E. W., 230 W. 113th St., New York City.
Shorey, Edmund C., Box 360, Honolulu, H. I.
Walker, Percy H., 416 McClury St., Huntsville, Ala.

Issued with September Number, 1900.

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Hegeman, John W., 102 Barbey St., Brooklyn, N. Y.
Hooper, Everett D., 10 Studio Building, Boston, Mass.
Porter, Horace C., 902 Locust St., Kansas City, Mo.

CHANGES OF ADDRESS.

Enright, Bernard, 330 E. 4th St., South Bethlehem, Pa.
Goldstein, Harris, care J. W. Preston, Tyler St., Depew, N. Y.
Hibbard, P. L., 525 Clayton St., Waukegan, Ill.
Kendall, E. Dwight, 1109 Park Pl., Brooklyn, N. Y.
Leach, Miss Mary F., 74 Pitcher St., Detroit, Mich.
Lenher, Victor, Univ. of Wis., Madison, Wis.
Stursberg, J. A., care W. Stursberg, Schell & Co., 79-81
Leonard St., N. Y. City.
Thompson, Firman, New Carlisle, O.
Wolfe, J. V., Pekin, Ill.

ADDRESS WANTED.

Welt, Miss Ida, formerly of 814 Lexington Ave., N. Y. City.

MEETINGS OF THE SECTIONS.

RHODE ISLAND SECTION.

The annual meeting of the Rhode Island Section of the American Chemical Society was held June 13, 1900, at Kingston, R. I.

The Section was entertained by Dr. J. H. Washburn, president of the Rhode Island College of Agricultural and Mechanical Arts.

The following officers of the Section were elected for the year 1900-1901 :

Presiding Officer, Walter M. Saunders ; Secretary and Treasurer, Walter E. Smith ; Member of the Executive Committee, Charles M. Perry.

WALTER E. SMITH, *Secretary.*

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Hicks, Walter T., 300 S. Broadway, Los Angeles, Cal.
Johnson, Charles M., 701 Orchard St., Avalon, Pa.
Rademacher, Hermann A., Box 243, Lawrence, Mass.
Rogers, Herbert F., Provident Chem. Wks., St. Louis, Mo.
Vosburgh, C. H., High School, Jamaica.

NEW MEMBERS ELECTED AUGUST 24, 1900.

Harrington, Charles, Harvard Med. School, Boston, Mass.
Harris, Isaac F., Chapel Hill, N. C.
Jürgensen, Dr. Rolof, care Dr. Jürgensen and Bauschlicher,
Tech.-Bureau für die Chem.-Industrie, Prag-Zizkov, Austria.
Shepard, C. H., Pinole, Contra Costa Co., Cal.
Smith, Lyman, G., Roxbury High School, Warren St., Boston, Mass.
Smith, Thorn, Isabella, Polk Co., Tenn.
Wainwright, John W., M.D., 177 W. 83rd St., N. Y. City.
Young, Clare C., 518 Alvarado, Los Angeles, Cal.

ASSOCIATE ELECTED AUGUST 24, 1900.

Medcalf, Geo. T., Box 280, Eureka, Humboldt Co., Cal.

CHANGES OF ADDRESS.

Adams, Maxwell, 5815 Drexel Ave., Chicago, Ill.
Best, Otto, Bay & Dupont Sts., San Francisco, Cal.
Brown, H. F., Int. Sm. Powder & Dynamite Co., South
Amboy, N. J.
Culmann, Julius, 400 W. 153rd St., N. Y. City.
Dailey, J. Glanding, care Ledoux & Co., 99 John St., N. Y.
City.
Goldstein, Harris, 228 Henry St., N. Y. City.
Grabfield, Jos. P., Medinah Temple, cor. Jackson and 5th Ave.,
Chicago, Ill.
Hummel, John A., Agr. Expt. Sta., St. Anthony Park, Minn.

Kendall, Robert E., 46 Maple St., Glens Falls, N. Y.
Loeser, R. M., Palo Alto, Cal.
Mabery, C. F., 57 Adelbert St., Cleveland, O.
Moyer, J. Bird, 5116 Arch St., Philadelphia, Pa.
McKenzie, R. Monroe, Rahway, N. J.
Peppel, S. V., 169 King Ave., Columbus, Ohio.
Phalen, W. C., Socorro, N. M.
Sovereign, C. L., Glucose Sugar Ref. Co., Davenport, Iowa.
Tucker, Chas. W., Grant & Farragut Roads, Swampscott,
Mass.
Tufts, J. L., Gen. Chem. Co., Laurel Hill Works, Laurel
Hill, N. Y.
Walker, Percy H., Fayetteville, Ark.

ADDRESS WANTED.

Goodell, George A., formerly of 284 St. Nicholas Ave., N. Y.
City.

ERRATUM.

By an oversight the name of Dr. Talbot did not appear in the list of councilors present at the meeting of the council in New York last June. He was present, and his name should be added to the list of those councilors who attended the meeting.

Proceedings.

COUNCIL.

The motion printed on page 74 of the Proceedings has been amended so as to read as follows :

Resolved, That the president of the Society appoint a committee of five, of which he himself shall be one, to report to the Council upon a new contract for the printing of the Journal of the Society.

It has also been voted that the present contract for printing the Journal be continued till such time as a new contract can be presented and approved.

NAMES PROPOSED FOR MEMBERSHIP.

Balcom, Reuben W., Mass. Inst. Tech., Boston, Mass.
Baltzly, Edwin B., Perth Amboy, N. J.
Benedict, Francis G., Middletown, Conn.
Braman, Winfred W., Durham, N. H.
Breves, Rudolph, Rahway, N. J.
Brown, John W., 126 Massachusetts Ave., Boston, Mass.
Champion, E. C., Iola Portland Cement Co., Iola, Kans.
Gordon, A. S., Oliver Iron Mining Co., Mountain Iron, St. Louis Co., Minn.
Grainger, Wm. E., Cranberry, Mitchell Co., N. C.
Hemmings, Frederick J., 12 Pearl St., Boston, Mass.
Heckeroth, Wm. C., 3443 N. 18th St., Philadelphia, Pa.
Heckman, J. Conrad, Larkin Soap Co., Buffalo, N. Y.
Melcher, Arthur C., 58 Bowen St., Newton Centre, Mass.
Morgan, W. C., Washburn College, Topeka, Kans.
Osgyani, Arpad, 64 Orchard St., Astoria, L. I., N. Y.
Pough, Francis H., 146 Hicks St., Brooklyn, N. Y.
Walton, James H., Jr., Room 317, 126 Massachusetts Ave., Boston, Mass.
Wheeler, Alwyn S., Chapel Hill, N. C.
Woods, Chas. D., Orono, Me.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Cary, Edward A., Lafayette College, Easton, Pa.
Felt, W. W., 9431 Normal Ave., Chicago, Ill.
Haskell, Albert A., Essex, Mass.
Howard, John J., 118 McKeen Hall, Easton, Pa.

NEW MEMBERS ELECTED SEPTEMBER 17, 1900.

Hegeman, John W., 102 Barbey St., Brooklyn, N. Y.
Hooper, Everett D., 10 Studio Bldg., Boston, Mass.
Porter, Horace C., 902 Locust St., Kansas City, Mo.

CHANGES OF ADDRESS.

Affelder, Oscar I., 1230 Sheffield St., Allegheny, Pa.
Archibald, Eben H., 1691 Cambridge St., Cambridge, Mass.
Ashley, Harrison E., care Tremont Nail Co., West Wareham, Mass.
Barrows, W. A., Jr., Everett, Bedford Co., Pa.
Baxter, Gregory P., Swarthmore College, Swarthmore, Pa.
Beans, H. T., Univ. of Idaho, Moscow, Idaho.
Bonnet, Frederic, 9 Wadsworth House, Cambridge, Mass.
Bowman, Walker, 538 W. 14th St., New York City.
Cayvan, L. L., 294 W. Monroe St., Chicago, Ill.
Chesnut, Victor K., U. S. Dept. of Agr., Washington, D. C.
Condit, Louis C., 85 Newkirk Hall, Lafayette College, Easton, Pa.
Cook, A. D., 519 E. State St., Ithaca, N. Y.
Craig, A. G., 5803 Parker St., Pittsburg, Pa.
Cuadrado, Gaston A., Dept. de Anal. Quimico, Monte 44, Habana, Cuba.
Dodge, F. E., care Barrett Mfg. Co., Tucker and Bermuda Sts., Frankford, Philadelphia, Pa.
Dunlap, Frederick L., 616 Church St., Ann Arbor, Mich.
Duryea, Chester B., 34 Gramercy Park, N. Y. City.
Williams, S. Everard, 4 Brimmer St., Boston, Mass.
Fuelling, J. L. Industrial Tablet & Chemical Co., Mercer St., Mill Road, Jersey City, N. J.
Green, Erik H., 41 St. Botolph St., Boston, Mass.
Havens, Franke S., 30-32 Varick St., New York City.
Hollis, Frederick S., Med. Dept., Yale Univ., New Haven, Conn.
Huntington, Harwood, Buckingham, 2 E. 50th St., New York City.
Johnson, T. B., Sheffield Chem. Lab., Yale Univ., New Haven, Conn.

- Knight, George W., 39 Front St., Schenectady, N. Y.
 Knorr, A. E., care Guggenheim Sm. Co., Perth Amboy, N. J.
 Laudig, O. O., Supt. Blast Furnace, care Ill. Steel Co.,
 Joliet, Ill.
 Ledoux, A. R., 99 John St., New York City.
 Lipman, J. G., 616 N. Aurora St., Ithaca, N. Y.
 Lysle, Walter S., 507 W. 112th St., New York City.
 Merigold, B. S., Worcester Poly. Inst., Worcester, Mass.
 Meyer, Gustave M., care Bigler & Moriand, 6 Rue St. Legers,
 Geneva, Switzerland.
 Miller, John A., 44-45 Lewis Block, Buffalo, N. Y.
 Millwood, James P., 246 Willoughby Ave., Brooklyn, N. Y.
 Macdowell, W. F., U. S. Marine Hospital Service, Havana,
 Cuba.
 McIntosh, Douglas, Chem. Bldg., McGill Univ., Montreal,
 Canada.
 Norman, Geo. M., 249 Center St., Bloomsburg, Pa.
 Norton, Mrs. Alice P., 230 Hampden St., Chicago, Ill.
 Parmelee, C. W., N. Y. and Boston Dyewood Co., Green-
 point, Brooklyn, N. Y.
 Peek, R. L., 99 John St., New York City.
 Peppel, S. V., 169 King Ave., Columbus, O.
 Phelps, Isaac King, 102 North, Yale Univ., New Haven,
 Conn.
 Porter, Miss Georgia, care Johnson & Johnson, New Bruns-
 wick, N. J.
 Root, Wm. W., Chicago Manual Training School, Chicago,
 Ill.
 Sanderson, John, 4 Lancaster Road, London, N. W., England.
 Sawyer, Harris E., 27 Bellevue St., Dorchester, Mass.
 Smither, F. W., 36 Cole Bldg., Nashville, Tenn.
 Sy, Albert P., Frankford Arsenal, Frankford, Philadelphia,
 Pa.
 Taylor, Thomas M., 3607 Sansom St., Philadelphia, Pa.
 Thurlow, Nathaniel, 43 Halsey St., Newark, N. J.
 Tuschka, Otto, Fundicion No. 2, Monterey, Mexico.
 Watson, E. T., 935 Neil Ave., Columbus, Ohio.
 Whittier, Charles T., 92 St. James Pl., Brooklyn, N. Y.



ROBERT WILHELM BUNSEN.

PROFESSOR R. W. BUNSEN.

The committee¹ appointed at the Columbus Meeting of the American Chemical Society to draw up a memorial upon the late Professor R. W. Bunsen, an honorary member of the Society during nearly the whole period of its existence, presents the following as a tribute of the Society and of American chemists generally to the life, character, and works of that great man and eminent chemist.

Robert Wilhelm Eberhard Bunsen was born in Göttingen on March 31, 1811. Among his ancestors one of the most prominent was Jeremiah Bunsen, who lived in Arlosen, 1688-1752, and was Hofmaler, Münzmeister, and Bürgermeister there. He was a great admirer of natural science, and himself published certain writings on electricity, magnetism, the Northern Lights, etc.

Little is known of Robert Bunsen's childhood and youth. He was the youngest of four sons of Christian Bunsen, librarian and professor of philology in the University of Göttingen. The father was a man of cheerful disposition and a ready sense of humor. His mother was the daughter of a British officer of Hanover,—Quensel,—a woman possessed of depth of mind and heart. It is not difficult to see that some of the characteristics of both parents were freely transmitted to the son. As a boy, Bunsen is said to have been of a quick and violent temper, which his mother only knew how to control, but those who knew the man could scarcely be brought to give credence to such rumor. If true, however, how great must have been the self-mastery that changed him into the serene and quiet man of his mature years! At home Bunsen had excellent opportunities to learn languages other than his native tongue, from the number of foreign youths, especially French, who frequently visited his parents and sometimes lived in the family. This was a very fortunate circumstance and early became of great practical utility to him. At the age of seventeen he passed his matriculation examination for the University, and when nineteen took the degree Doctor of Philosophy. He had a good classical education and even to his old age was fond of reading Cicero and other Latin authors in the original. In 1830 he won an academic prize for an exhaustive enumeration and description of hygrometers, written in elegant Latin. This paper seems also to have served as his inaugural dissertation upon the attainment of his doctor's degree.

At the University he was quiet and retiring and took but little

¹ The committee has made free use of every available source of information regarding Professor Bunsen, and has endeavored to give credit for all important quotations, although it has not seemed necessary to indicate with quotation marks simple data of statistics and facts.

part in what is generally understood as student life. He was full of good humor, however, and a diligent and enthusiastic student. His special subjects of study were physics, chemistry under Stromeyer, mineralogy and geology under Hausmann, and mathematics under Gauss. He was especially fond of geognostic studies and made frequent excursions in the vicinity of Göttingen and in the Harz. These excursions for practical study and observation he began even before he entered the University.

In May, 1832, Bunsen undertook an extended tour for the sake of broadening his scientific information and culture. He went to Berlin, Paris, and Vienna, making a large portion of the journey afoot, visiting chemical manufactories and other works at various points en route, and taking many opportunities to extend his geognostic observations. During this tour he formed the acquaintance of many of the leading scientists of his day, and enjoyed more or less intimate association with a number of them. He met Runge, Gustav and Heinrich Rose, and Mitscherlich, and was with the latter for three weeks pursuing geognostic studies in the Eifel. In Giessen he met Liebig and Wöhler, and in Paris Pelouze, Regnault, Brogniard, and others. He studied the mineral and geological collections of Weiss and for a time worked in the laboratory of Heinrich Rose. It was under the advice of Rose that he went to Paris. While in Paris he attended a session of the Academy at which Chevreul, then at the summit of his fame, presented a paper upon cholera and its treatment. At this session also it was announced that Ampère had found in hydrofluoric acid a specific for combatting the disease. Bunsen, through the recommendation of prominent scientists, gained admission to the Polytechnic School, where he attended a course of lectures during the winter semester, 1832-1833. He made no attempt to attend lectures in Berlin and Vienna, but preferred to extend his scientific knowledge and opportunities by acquaintance and association with the learned men whom he met. In this he succeeded to a remarkable degree, and he dated a life-long acquaintance and deep friendship with Heinrich Rose, Mitscherlich, and others from this tour. He remained in Paris from the last of September till the middle of May and then went to Vienna *via* Innsbruck and Salzburg. His stay in Vienna lasted about six weeks, after which he returned to Göttingen, stopping on his way at Prague, Freiberg, and Leipsic.

The object of Bunsen's tour had been most successfully attained. He had come into personal acquaintance with great scientists of Europe, and by their aid and friendship had had opportunities for the study of theoretical and applied science, which helped to lay broad, deep, and solid the foundation upon which his success and fame were to be built. Already he was a

marked man and many eyes were looking toward his future. Returning to Göttingen, he became privatdocent in 1833, and after three semesters, upon the death of Stromeyer, he conducted the lectures at the University upon theoretical and practical chemistry. His popularity was great, as was shown by the number of students in attendance. In January, 1836, Wöhler was called to become the successor of Stromeyer, at Göttingen, and Bunsen was appointed Wöhler's successor as professor of chemistry in the Polytechnic School at Kassel. This institution had long been known for the character and standing of its professors, and Bunsen did his part in sustaining its reputation. He entered upon his work at Kassel with great vigor and made an enviable record during the short period of his stay there.

In 1838, Bunsen accepted a call to the University of Marburg, where he remained thirteen years as professor and director of the chemical laboratory. In 1851, he went to the University of Breslau, where he planned a famous working laboratory, and the next year he accepted a call from Heidelberg, at that time the goal of every German professor's ambition, and "the *ne plus ultra* of his promotion." Here he planned a new laboratory which, when completed in 1855, was the largest in all Germany, furnishing working places for fifty students. Here it was that students from all quarters of the world thronged and crowded upon one another to secure the opportunity of attending the lectures and obtaining personal instruction in laboratory practice and research from the now renowned professor. Bunsen remained at Heidelberg until the day of his death, repelling all overtures from Berlin when the German government was putting forth its most strenuous efforts to make the university of that city the greatest seat of learning in all Europe. He retired from active work in 1889, having filled the position of teacher for more than fifty years, during which period all his important work as a scientist was also accomplished. His death occurred August 16, 1899.

In 1834, Bunsen, in conjunction with his colleague Berthold, published the results of his first scientific investigation, and by that means conferred a lasting boon upon humanity. He announced that moist, freshly precipitated ferric hydroxide is a sure antidote in cases of arsenical poisoning, providing it is given early enough and in sufficient quantity. This paper at once attracted wide attention on account of the great and permanent importance of the remedy which is to-day almost universally known and accessible.

In 1835, Bunsen investigated some of the compounds which the double cyanides form with ammonia. He measured the angles of the crystals which many of the cyanides form and estab-

with the different metals as electrodes, and analyzed the light with a prism. In that way, in 1844, some years before the invention of the spectroscope, he obtained and described the true line spectra of various elements. For many years after this, Bunsen's investigations in spectrum analysis were interrupted by other matters, and when he renewed his researches in this direction, it was with the aid of the gas-burner which he had meanwhile devised, and later with the additional aid of the spectroscope, the joint production of the inventive genius of himself and his collaborer, Kirchhoff.

In 1857, Bunsen and Roscoe first described the Bunsen burner. This invention furnished a non-luminous gas flame, of relatively high temperature, in which chemical substances could be vaporized and a spectrum obtained due to the luminous vapor. This burner is now used as a source of heat in various manufacturing processes, and in many households, and is practically indispensable in all chemical laboratories. With the invention and use of this burner, a new impulse was given to the investigation of the spectra of the metals, and Bunsen now studied them from their chlorides, as these were volatilized in the colorless flame of the burner. Kirchhoff, professor of physics at Heidelberg, became associated with him in these researches, and dealt more especially with the physical problems involved, while Bunsen approached the subject from the standpoint of a chemist who was also an expert in various phases of physical research.

In 1859, Bunsen and Kirchhoff perfected the spectroscope and continued their classical researches in spectrum analysis, among other results discovering the metals caesium and rubidium, the salts of which were obtained in small quantity, but in the hands of Bunsen in sufficient amount to enable him to determine many of the properties and constants of these rare metals. By evaporating 44,000 kilos of the Dürkheim mineral water in which traces of these two metals had been found, he obtained 16.5 grams of the mixed chlorides of the two new metals, and with this he succeeded in separating them and in establishing their relationship so well that his results still stand as practically correct and complete.

The invention of the spectroscope, the founding of the science of spectrum analysis, and the important researches in that science which were conducted by Bunsen and Kirchhoff, led to far-reaching results and were alone sufficient to place the name of each of these investigators upon the pinnacle of enduring fame. From the record that has already been made by this new method of research, we are warranted in saying that it would require the boldest flights of scientific imagination

to encompass the variety and extent of the uses to which the spectroscope may be applied and of the revelations which may be expected from spectrum analysis. In fact it has already thrown floods of light upon nearly every department of theoretical science and has furnished one of the keenest and most penetrating of instruments which man can use in the application of science to practical affairs, and to the investigation of unexplored fields of scientific research. A catalogue of its revelations in optics, astronomy, and chemistry and of its application in medical and medico-legal practice and in the arts and manufactures, would be wearisome from the mass of important details it would present, and we can best leave this topic by assuming that its principal facts and outlines are to-day familiar to every well-informed person.

Bunsen's work in connection with the spectroscope and spectrum analysis constituted only a portion of his researches upon light. Just as the investigations of the line, absorption and spark phenomena were of far-reaching scientific importance and have been turned to practical account in a great variety of directions, so his researches upon the chemical action of light have been regarded as "the classical model for all later investigations in the realm of physical chemistry" and have been of great practical value in considerations affecting photography, agriculture, and various other arts and industries, while his method of measuring the intensity of light from any given source, is of great importance from a scientific standpoint and has its valuable application in the Bunsen photometer as used to-day in determining the candle-power of illuminating gas and the electric light.

The variety and accuracy of Bunsen's analytical methods are marvelous. It has been said that "next to Heinrich Rose he was the greatest and especially the most original analyst of his time." There are those, however, who would not make even this exception in favor of Rose, especially when Bunsen's manipulative skill, the certainty and accuracy of his results, his many ingenious devices, and the simplicity of the apparatus he designed for doing his work are taken into consideration. We have only to mention his gasometric and volumetric methods, his flame reactions, distinct from the spectrum analysis, his analyses of silicates and mineral waters, separation of arsenic and antimony, separation of the rare earths and the metals of the platinum group, to recall these and scores of other processes with which every chemist is to-day familiar, which he employs in his own work whenever occasion may arise and for many of which no adequate substitute is yet known.

No important branch of chemistry remained unexplored by

Bunsen, and his accomplishments in any one of them alone would have secured for him abiding fame. Organic, inorganic, physical, analytical, theoretical, and technical chemistry were alike enriched by his researches and his name is connected in some way with our knowledge of almost every element known in his day. Chemical and other scientific laboratories to-day are full of apparatus and contrivances invented by Bunsen, and they have become practically indispensable in many lines of modern scientific research. No chemist or physicist now would think of carrying on his investigations without them. But the realms of chemistry and physics were not broad enough to circumscribe the genius and labors of Bunsen. He enriched every field which he entered as a scientific investigator and he entered fields of investigation in nearly every science. Chemistry, physics, and mineralogy, it is true, absorbed the greater portion of his time, thought, and energy, but the results he achieved in these were so fundamental and far-reaching that astronomy and various other branches of pure and applied science reaped a full and rich harvest as the ripened fruit of his labors.

It has been said that "it never once happened to Bunsen to take up any considerable research without producing a discovery decidedly brilliant; and he almost always flung in something useful to boot." This was eminently illustrated by his researches on cacodyl and the discovery of ferric hydroxide as a remedy for arsenical poisoning; by his analysis of blast-furnace gases, revealing the waste of gaseous fuel and pointing the way to more economical working through the use of the hot blast and the development and use of producer gas; and by his investigations in the realm of optics, leading to the invention of the spectroscope and the valuable results which have flowed from spectrum analysis.

Bunsen was a scientific genius of the highest order, whether we define the term genius as the capacity for work, or as the ability to perceive and recognize truth and bring to light fundamental facts and laws when buried beneath the rubbish of false theory and tradition or concealed by a mass of details which permit none but the most penetrating intellect to discover them and to bring them to the comprehension of ordinary minds and within the range of ordinary human experience. He was not himself very tolerant of theories. He said, in 1871, to one of his pupils, that he had already lived through three or four sets of theories and he expected to see many more before he died.

Bunsen used almost every discovery and investigation he made as a basis for further work, and it seemed as though every advance opened to him vistas ever more and more alluring. The good uses to which he put his battery and burner, the employment

of magnesium in his investigations on light and the thoroughness with which he worked out the properties of the metals he reduced, and various data regarding them, all testify to the completeness and comprehensiveness of his work. He never left much for others to do in the fields in which he labored. "He left the theme he chose completed." While following up a single line of investigation, he would often stray into by-paths in which he would pluck the ripened fruit with which nature tempted him, and strengthened and inspired by that he would return with broader data and fuller insight into the main line of his investigations as a reward for his little side trip. Many a person would have been distracted by the varied secrets which nature yielded to him at such times and might have been turned from the main subject of their inquiry by inviting side issues; but while Bunsen gave much attention to these, they always strengthened him in his main work while, at the same time, yielding abundant harvests and furnishing both the incentive and the foundation for subsequent investigations in kindred lines.

Bunsen's methods were precise, accurate, and thorough. His fondness for mathematics and his early education under Gauss in that direction, gave a decidedly mathematical turn to all his researches, and even the simpler reactions of the chemical laboratory were regarded by him from a mathematical point of view. This method of looking upon his work did not invest the subjects with greater obscurity, but just the reverse. The harmonious and fundamental relations of mathematics illumined the whole subject he was investigating, and so clarified the atmosphere as to render his methods charmingly simple and accurate. One can hardly say whether his mind was more successfully inductive or deductive in its processes. There was in its working a rare and happy facility in the use of both, and such a combination of them as rendered his investigations intuitively clear and direct, yet fundamental and comprehensive, and such as would satisfy the demands of formal deductive reasoning. His manipulations, methods of analysis, and construction of apparatus were but the outward and natural expression of the operations of his comprehensive and penetrating intellect.

Bunsen's greatness as a man and as a personal companion and friend is in no danger of being eclipsed by his world-wide renown as a scientific investigator, so long as the testimony of those who knew him can be called in evidence. Physically he was over six feet in height, of massive proportions and swarthy complexion. His personal address was so cordial and unaffected and the charming smile which illumined his features so capti-

vating that all whom he met were irresistibly drawn to him and loved to linger in the atmosphere of his presence. His pupils almost worshiped him for his genius and achievements, loved him for his fatherly ways and his interest in them and their work, and were frequently drawn into the closer relation of personal friendship by his generous nature and the childlike simplicity of his manner. In some instances these relations were lifelong and intimate, but whether circumstances rendered this possible or not, the kindest feelings of affection for Bunsen as a man, and a high estimate of his genius as a scientist and a teacher, were the permanent possession of those who worked with him in the laboratory and attended his lectures. "In that epoch-making book in literature and science entitled 'Heat as a Mode of Motion,' one of his former pupils has recorded his appreciation of Bunsen in the following language: 'To his friend and teacher, Robert Bunsen, this book is dedicated by John Tyndall.'" Roscoe, who, while a pupil, was very intimately associated with Bunsen in his investigations on light, says: "It is only those who have had the benefit of working under and with him who can fully understand the feeling of affection and respect with which his pupils regard his memory."

From some of his American pupils we quote the following expressions of appreciation, reminiscences, and estimates of Bunsen and his work:

"His name is dear and sacred to us all."

"I shall never forget his kindly patience and helpfulness. That sweet smile of his is ever present with me."

"I shall always remember with pleasure his fatherly ways and great interest in his pupils."

"I have many of the pleasantest recollections of the dear old gentleman who was most kind and gracious to me both in and out of the laboratory."

"To those whose good fortune it was to become an intimate, his nature unfolded, and close and devoted friendships were formed."

"His unaffected simplicity, genial nature, and most lovable disposition were marked characteristics which no one who came in contact with him as a pupil could fail to note. His interest in the work of his pupils was intense and sometimes manifested itself in unexpected ways. He was at all times an honest, faithful, and earnest searcher after truth, and never seemed conscious of any feeling of superiority over his humblest pupil. To know him was to love him. It would, indeed, be difficult to tell which feeling would be uppermost in one's memory of this truly great yet distinctly childlike man—admiration for his achievements or veneration for his character."

"Nothing could win a student's heart more quickly than the gracious way in which he would initiate the beginner into flame reactions, except it might be the delight it gave him to conduct an advanced student through the mazes of a mineral water or platinum ore analysis, or the charm he would throw about his methods of exact measurement, as in the graduation of a eudiometer, the making of an elaborate gas analysis, the determination of the specific heat of a solid, liquid, or gas, or the mapping of spectra."

"I could write of the enthusiastic reception of Professor Bunsen by his students as he appeared at the door of his lecture room, the inspiration his presence made as he gave suggestions at the laboratory tables, his marvelous skill in chemical manipulations, his simple, patient way of illuminating for a student what had been an obscure subject, the crisp words of commendation for a bit of good work done, the feeling near to worship that came to his pupils; but these facts are, I suppose, the common knowledge of all his students."

"As a student I felt I was alongside of a kind-hearted big boy who knew immensely more than I did, and was only too anxious to help me in need. We felt he was interested in our work and was not only capable of assisting us but was ready at a moment's call to help and to advise. I felt that I was getting from him far more personal attention than I deserved. He was one of us in in our working hours and was anxious to bring each labor to a successful result. He lost nothing in professional dignity thereby. We never presumed at familiarity. To us he was ever Robert Bunsen, Geheimrath, and we kept our places 'with our hands on our mouths and our mouths in the dust.'"

"As to the inspiration I derived from two semesters of close contact with him, it was worth all my years elsewhere."

"He was a prince among teachers, simple, plain, and clear, and admirable in his experimenting. The only notes he used were mathematical data written upon a small blackboard at his left hand. In the working laboratory he was always patient and gave us personally a great deal of attention, more than we got anywhere else."

"I first met Bunsen in the retired valley of Engelberg, Switzerland, in 1863. Learning by accident that he was at an adjoining Gasthaus, I called on him and told him of my plans to continue my studies in Heidelberg. He received me graciously and immediately won my heart by his affability, by the charming smile that lit up his large features, and by his unselfish interest in my personal affairs."

"I first met Professor Bunsen, November 6, 1855. I had gone to Germany to study chemistry under him and Liebig, and the

day of my arrival at Heidelberg I called on him at his rooms in the new laboratory building. This was then considered the largest and best arranged in the world. I found him smoking his after-dinner cigar and I immediately took a liking to him. He was then in the prime of life, forty-four years old, and his genial but earnest face impressed me. He seemed younger than I had expected. He had many questions to ask about chemical instruction in America, for students from this country were then flocking to the German University. There were then between fifty and sixty students in his laboratory, scarcely more than half of them German. It seemed to me that half of the nations of the world were represented. Bunsen was genial with his students, visiting everyone's table in his daily circuit of the working rooms, having something to say to each one about his work, even if but a word, but would generally linger if properly tempted. He gave his lecture on general chemistry at nine o'clock in the morning. His method was clear, logical, and concise. He would begin his lecture from the standpoint of our present knowledge of the subject he was discussing, commencing with the element and following by logical succession the chemistry of its compounds."

"Just after the Christmas recess he invited his students to a dinner at the Badischer Hof. It was a happy occasion. There were a few short speeches and he seemed doubly genial. In those days a good cork was a prize for laboratory use, and when on that occasion he caught me slipping a champagne cork into my pocket, with a twinkling eye he remarked that I had the true laboratory instinct. As the dinner broke up he carefully gathered up and carried the other champagne corks away in his pockets, remarking to a student that champagne corks should never be wasted."

"At the opening of my third term, I was elected 'Polizei.' One of the events of my official life was regarded as an exhibition of unparalleled audacity of which only an American was capable. I fined Hofrath Bunsen, who, after lighting his cigar at the flame of a Bunsen burner, had left the gas burning and gone out of the room. According to custom and much to the consternation of the students, I chalked on the desk that Bunsen had used, the words 'six kreutzers' over my initials—a notice that could not be erased until the fine was paid. The next day when Bunsen approached the desk, he glanced at the inscription, smiled broadly, and to the amusement of the crowd of students that had gathered to see the result of my daring, opened his purse and handed me six kreutzers, with a pleasant commendation of the fidelity of the 'Polizei.'"

"After every lecture Bunsen rarely missed spending several

hours in the laboratory, going from student to student with inquiries, suggestions, and useful hints. Desirous of securing my share of this personal contact, I soon found the best way of inducing the Hofrath to linger was to have a supply of clean test-tubes and beakers on an orderly desk, with a query or two requiring experimental answers."

"While Bunsen rarely met his students outside the laboratory, he captivated each by the deep personal interest he took in their individual work. Indeed, so intense was his devotion often to their themes that it was not uncommon for a pupil to find on coming in the morning an analysis or process several stages more advanced than when it was left the night before. Bunsen was an early riser as well as a late worker, and between the two found ample time to have a 'finger in the pie.'"

"Bunsen's practical side is best known to the average man. He was a craftsman beyond compare in the details of what was needed in laboratory utensils and manipulative skill, as was evinced by simplicity of construction, neatness of procedure, and accurateness of result."

"As to his contributions to chemistry, they were enormous, and you must bear in mind that he was born in 1811 and that many of the devices of the laboratory, and most of the principles of the science of chemistry which we are teaching now as a sort of matter of course, 'things that go without saying,' were utterly unknown when he was graduated in Göttingen in 1830."

"In everything Bunsen attempted he was never satisfied until he had finished his work and put it upon an exact scientific basis. I have good cause to think him the best teacher I have ever had and the best chemist of his generation."

"Bunsen became an integral part of Heidelberg and the prestige of this university was to a considerable extent dependent upon his individuality. It was at this seat of learning that he made his most important discoveries and drew men from all parts of the world to his laboratory. Admirable as his previous work had been, it was amidst the charming natural surroundings there and in daily contact with such minds as Helmholtz, or his devoted coworker Kirchhoff, or in the genial companionship of Kopp and Hesse that his genius expanded. It was quite in keeping with his nature that others should partake of the infinite pleasure he had experienced, and he gladly initiated them into the skillful methods his resourceful mind had developed."

"Nothing so much marks Bunsen as a chemist of a past generation as the fact that one cannot speak of him as especially distinguished in any particular branch of the subject. If we go over the men of our science who are well known to-day we find that nearly every one is very closely identified with organic,

analytic, physical, or some other department of chemistry, and has done very little of note outside of his particular field. Bunsen did so much valuable work in every branch of chemistry that he was distinguished in all."

LIST OF AMERICANS WHO HAVE STUDIED UNDER PROFESSOR R.
W. BUNSEN.

The following list is, beyond doubt, incomplete, especially as to those who simply attended Bunsen's lectures without working in his laboratory, as was a common custom with medical students in particular. An attempt has been made to communicate with each living person whose name appears in the list. In a number of cases the letters of inquiry have elicited no response, and the information, obtained at second-hand and often meager, has thus been impossible of verification or extension. It is believed, however, that so far as concerns those who at one time or another worked in Bunsen's laboratory, the list is nearly complete.

Of the 101 persons enumerated at least 62 have either taken the doctor's degree under Bunsen or have at one time or another filled professional chairs at one or more institutions of learning, or both. Of the above 62, there are known to have taken the degree 33, and to have become professors 46. A number of the latter took their doctor's degree elsewhere. Death has claimed at least 20.

Andrus, Geo. Lawrence. (Brooklyn, N. Y.) 1873-74. Present address unknown. Did not pursue chemistry as a profession.

Austin, W. Lawrence. 1871-74. Ph.D., 1876. Metallurgical engineer, Denver, Colo. (Box 941).

Bache, Chas. L. 1869-71. Formerly with Philadelphia mint; now assayer and metallurgist, Redding, Cal.

*Bayne, H. A. 1875. At one time professor of chemistry, Royal Military College, Kingston, Ontario, Canada.

Becker, Geo. F. (New York.) 1868-69. Ph.D., 1869. Graduate Royal School of Mines, Berlin, 1871. Instructor University of California. Since 1879 connected with U. S. Geological Survey, Washington, D. C.

Bernays, A. C. 1872-73. M.D. Practicing physician in St. Louis, Mo.

Best, Wm. F. (Fredericton?, N. B.) About 1874-75. Has been analytical chemist in Nova Scotia or New Brunswick.

Blair, Geo. D. (Pittsburg, Pa.) 1870.

*Blake, Eli W. 1864. At one time professor of chemistry at the University of Vermont, again at Cornell, and later professor of physics at Brown University, Providence, R. I. Died 1895.

Bolton, B. Meade. (Richmond, Va.) 1883-84. M.D., University of Virginia, 1879. Formerly associate at Johns Hopkins, professor in Universities of South Carolina and Missouri; later director of the laboratory of hygiene, board of health, Philadelphia, Pa. Now practicing physician, Princeton, N. J.

- Bolton, H. Carrington. (New York.) 1863-65. Ph.D., Göttingen. Formerly assistant in Columbia School of Mines, professor Woman's Medical College of New York Infirmary, and Trinity College, Hartford, Conn. Present address Cosmos Club, Washington, D. C.
- Borden, Wm. F. (Chicago.) 1868. At one time engaged in metallurgical operations at Leadville, Colo. Present address Borden Block, Randolph and Dearborn Streets, Chicago, Ill.
- *Bowen, Henry C. About 1875. Instructor in School of Mines, Columbia College, N. Y., and technical chemist. Died 1899.
- Bowman, Walker. 1885. Ph.D., Berlin, 1888. At one time professor of chemistry, Ohio State University, now chemist Louisville Spirit Cured Tobacco Co., Louisville, Ky.
- Boyd, Wm. W. (Boston.) 1872?
- Brewer, Wm. H. (Poughkeepsie, N. Y.) 1855-56. Formerly professor Washington and Jefferson College, Washington, Pa., assistant on Geologic Survey of California, professor University of California. Since 1864 professor of agriculture, Sheffield Scientific School, New Haven, Conn.
- Brown, W. G. 1880-81. Formerly professor Washington and Lee University, Va., chemist Department of Agriculture, Washington, D. C.; now professor University of Missouri, Columbia, Mo.
- Burney, Wm. (Davidson, N. C.) Between 1875-79. Ph.D., 187-. Professor of chemistry, College of South Carolina, Columbia, S. C.
- Burton, Beverly S. 1871. Ph.D., 1871. At one time professor East Tennessee University. Retired from active chemical work. Address Munich, Carlsstr. 61aIII.
- Case, Jos.? Alliene? (Columbia, Pa.?) 1871?
- Caldwell, Geo. C. (Framingham, Mass.) 1857-58. Ph.D., Göttingen 1857. Formerly professor Antioch College, Ohio, and Agricultural College of Pennsylvania. Since 1868 professor agricultural and analytical chemistry, Cornell University, Ithaca, N. Y.
- Chapman, Nelson C. (St. Louis, Mo.) 1870-71. Has not followed chemistry. President Cumberland Construction Co., Chemical Bldg., St. Louis, Mo.
- Chatard, Thos. M. (Baltimore, Md.) 1876. Ph.D., 1876. Formerly chemist U. S. Torpedo Station, Newport, R. I., later U. S. Geological Survey. Not actively engaged in chemistry. Address 1714 Rhode Island Ave., Washington, D. C.
- Comey, Arthur M. (Boston, Mass.) 1884-85. Ph.D., 1885. At one time professor Tufts College, Boston, Mass. Address 54 Concord Ave., Cambridge, Mass.
- Dana, Edward S. (New Haven, Conn.) 1872-73. Ph.D., Yale. Professor Yale University, New Haven, Conn.
- De Fremery, James L. 1885-86. Ph.D., 1886. President and general manager of the American Lucol Co., 44 Broadway, New York City.
- *Dexter, Wm. Prescott, M.D. (Boston, Mass.) 1855. Died 1890.
- Dodge, Jacob A. (Salem, Mass.) Between 1875-79. Ph.D., 187-. Lately professor of chemistry, University of Minnesota. Present address unknown.
- Doremus, Chas. A. (New York.) 1870-72. Ph.D., 1872. Formerly professor University of Buffalo, N. Y., now assistant professor of chemistry and physics, College of the City of New York.

- Drown, Thos. M. (Philadelphia, Pa.) 1866-68. Formerly professor of chemistry, Lafayette College, Easton, Pa., and Massachusetts Institute of Technology, now president Lehigh University, South Bethlehem, Pa.
- *Easter, J. D. 1854. Ph.D., 1854. At one time professor of chemistry, University of Georgia, Athens, Ga. Died an Episcopal clergyman in Kentucky.
- Fisher, Davenport. 1854-55. Ph.D., 1854. Analytical chemist, Room 610, Old Insurance Building, Milwaukee, Wis.
- Fisher, Wm. Righter. (Philadelphia, Pa.) 1872. Attorney at law, Stephen Girard Building, Philadelphia, Pa.
- *Genth, F. A. (Waechtersbach, Hesse-Cassel.) Ph.D., 1846. Received degree at Marburg while Bunsen was professor there; was Bunsen's assistant three years prior to coming to America. Later professor of chemistry and mineralogy, University of Pennsylvania. Died 1893.
- Goodwin, W. L. 1880-81. D.Sc., Edinburgh, 1881. School of Mines, Kingston, Ontario, Canada.
- Goodyear, Henry. (New Haven, Conn.) 1870-71.
- Hague, Arnold. (Boston, Mass.) 1864-65. Assistant Geologist Fortieth Parallel Survey. Since 1879 member U. S. Geological Survey, Washington, D. C.
- Hale, Albert C. (New York.) 1879-80. Ph.D., 1880. Formerly president Colorado State School of Mines. Since 1883 head teacher physical sciences, Boys' High School, Brooklyn, N. Y. Address 551 Putnam Ave.
- *Hallock, Edward J. 1877-78. Ph.D., 1878. Assistant in chemistry, Columbia University, New York City. Died 1884.
- Hennessy, Walter. 1869-70. Lawyer, 299 Nassau Street, New York City.
- Hilgard, E. W. (Zweibrücken, Rhenish Bavaria.) 1852-53. Ph.D., 1853. Formerly state geologist, and professor of chemistry, University of Mississippi, professor of geology, etc., University of Michigan. Now professor of agriculture, University of California, Berkeley, Cal.
- Hillebrand, Wm. F. (Honolulu, H. I.) 1872-76. Ph.D., 1875. Formerly assayer, Leadville, Colorado. Since 1880, chemist U. S. Geological Survey, Denver, Colorado, and Washington, D. C. Since 1892 also professor of chemistry, National College of Pharmacy, Washington, D. C.
- Hitchcock, H. A. (Chicago.) After 1872.
- Hodges, Harrison B. (Boston, Mass.) 1873-74. Formerly technical chemist in Boston; later with U. P. R. R., Omaha, B. & O. R. R., Baltimore, Southern R. R., Washington, D. C.; now purchasing agent L. I. R. R., Long Island City, N. Y.
- Hodges, N. D. C. 1874-75. Formerly editor "Science"; now librarian Public Library, Cincinnati, Ohio.
- Hunter, Richard. (New York.) 1870.
- *Irby, Wm. (Virginia.) 1876-77. Ph.D., Bonn.
- Jackson, Chas. Loring. (Boston, Mass.) 1873-74. Professor of chemistry, Harvard University, Cambridge, Mass.
- Jayne, H. W. 1877-78. Ph.D., Strassburg, 1882. Address 931 N. Broad St., Philadelphia, Pa.
- Kinnicutt, Leonard, P. 1875-76. Director chemical laboratory, Worcester Polytechnic Institute, Worcester, Mass.

Kuntz. Between 1876-79.

Lees, Wm. T. (Brooklyn, N. Y.) 1873-76. Consolidated Gas Company, Avenue A., Corner 21st St., New York City.

Loeb, Morris. 1887-88. Professor of chemistry, University of the City of New York.

Luedeking, Robert. 1872-73. M.D., 1876, Strassburg. In 1882 lecturer, from 1883-92 incumbent of chair of pathological anatomy, since 1892 of chair of diseases of children in St. Louis Medical College (now a Department of Washington University), St. Louis, Mo.

*Lupton, N. T. (Nashville, Tenn.)? 1875. Formerly professor of chemistry, Vanderbilt University, Nashville, Tennessee, later in State University of Alabama. Deceased, Auburn, Ala.

Magee. (Philadelphia, Pa.) 1856.

*McBurney, Henry. (Boston.) 1864-65. Manufacturing chemist, Boston, Mass.

McCay, Leroy W. 1882. Ph.D., Princeton. Professor of chemistry, Princeton University, Princeton, N. J.

Merrill, N. Fred. (Charleston, ?.) 1871-72. Professor University of Vermont, Burlington, Vt.

Michael, Arthur. 1872-74. Professor of chemistry, Tufts College, Boston, Mass.

Miller, Geo. M. (New York.) 1863-65. At one time assistant in assaying, School of Mines, Columbia University, New York. Did not pursue chemistry afterwards.

Mixer, Wm. G. (New York.) 1872-73. Professor of chemistry, Sheffield Scientific School, New Haven, Conn.

Moellman, Rudolph. (Brooklyn, N. Y.) 1870.

*Moore, Gideon E. (New York.) 1870. Ph.D., 1870. Prior to 1867, analytical chemist, San Francisco, and assayer, Virginia City, Nevada. Chemist, Passaic Zinc Co., from 1872 to time of death in 1895.

Mayer, Benj. F. (New York.) 187-.

Nichols, Lyman. (Boston, Mass.) 1863-65. Has not followed chemistry. Address, 14 Commonwealth Ave., Boston, Mass.

Norton, Sidney A. (Bloomfield, O.) 1871. Ph.D., Kenyon, 1878. Formerly instructor Cleveland High School, professor of chemistry, Miami University, acting professor of physics, Union College. Since 1873 professor of chemistry, Ohio State University, Columbus, Ohio.

Norton, Thos. H. (Rushford, N. Y.) 1873-75. Ph.D. 1875. Formerly manufacturing chemist, Paris, France, professor of chemistry and librarian, University of Cincinnati, Ohio. Now U. S. Consul, Harput, Turkish Armenia.

*Osburn, 1874-75. Professor, Wittenberg College, Springfield, Ohio.

Penny, 1888. Was instructor in a Methodist College about 1891.

Pitman, S. Minot. 1873-74. At one time professor of chemistry, Tufts College, Boston, Mass.; now in insurance business, Providence, R. I.

Prochazka, Geo. A. (Newark, N. J.) 1873-74. Ph.D., 1874. Assistant in chemistry, Stevens Institute, Hoboken, N. J.; later analytical and consulting chemist, New York City; since 1881 technical and manufacturing chemist; now president Central Dyestuff and Chemical Co., Plum Point Lane, Newark, N. J. (Address 138 West 13th St., New York.)

- *Pugh, Evan. (Germantown, Pa.) 1856-57. Ph.D., Göttingen. Formerly president Pennsylvania State College. Died 1864.
- Rau, Henry M. 1877-79. Ph.D., 1879. chemist and chemical manufacturer, 130-132 Pearl St., New York City.
- Reese, Chas. L. (Baltimore, Md.) 1884-86. Ph.D., 1886. Formerly assistant, Johns Hopkins University, professor of chemistry, Wake Forest College, and South Carolina Military College, now chemist, New Jersey Zinc Co., Newark, N. J.
- Reynolds, Geo. (New York.) 1854-55.
- Rising, Willard B. (Mechlenburg, N. Y.) 1869-71. Ph.D., 1871. State analyst and professor of chemistry, University of California, Berkeley, Cal.
- *Root, Edward Walstein. 1864-65. Formerly assistant in chemistry, Columbia College, School of Mines; then professor of chemistry, Hamilton College, Clinton, N. Y. Died 1870.
- Seely, Henry M. (Onondaga, N. Y.) 1867-68. Formerly professor of chemistry, Berkshire Medical Institute, and Medical Department, University of Vermont; professor of chemistry and natural history, and since 1895, emeritus professor of natural history, Middlebury College, Vermont.
- Slingluff, Frank. (Baltimore, Md.) 1863-65.
- Smith, Eugene Allen. 1866-68. Ph.D., 1868. Prior to 1872 assistant on Geologic Survey of Mississippi, now state geologist and professor of geology and mineralogy, State University of Alabama, University, Alabama.
- Smyth, Geo. A. (Brunswick, .) 1872. Address 120 S. Grove Ave., Oak Park, Ill.
- Soule, Edward. (New Haven, Conn.) 1870.
- Springer, Alfred. 1871-73. Ph.D., 1872. Manufacturing chemist, Cincinnati, Ohio (Box 621).
- Strauss? Fred. (Pittsburg.) 187-.
- Terry, N. W. 1871-72. Ph.D., Göttingen. Professor of physics, U. S. Naval Academy, Annapolis, Md.
- Thomson, Wm. J. (New Orleans.) 187-.
- Treadwell, Fred. P. (Portsmouth, N. H.) 1875-79. Ph.D., 1878. Was Bunsen's lecture assistant for three semesters 1878-79. Ordentlicher professor of chemistry, Eidgenös. Polytechnikum, Zürich, Switzerland.
- Waddell, John. 1883-84. Ph.D., 1884. Professor of chemistry, School of Mines, Kingston, Ontario, Canada.
- Wahl, Wm. H. 1867-68. Ph.D., 1868. Secretary, Franklin Institute, Philadelphia, Pa.
- Waldstein, Martin. (New York.) 1873-75. Ph.D., 1875. Manufacturing chemist, 107 Murray St., New York City.
- *Walton, Henry C. (New York.) 1870. Died in New York.
- *Walz, Isidor. (New York.) 1866-68. Ph.D., 1867. Consulting and analytical chemist. Died in New York, 1877.
- *Webster, . (Pawtucket, R. I.) 1856. Died about 1860 or 1861, shortly after applying for a professorship in Washington and Jefferson College, Washington, Pa.
- Wilkins, Ross. 1879-82. Ph.D., 1882. Has held various positions as

chemist, assayer, and superintendent; now chemist Detroit plant, American Radiator Co., Detroit, Mich.

*Williams, Geo. H. (Utica, N. Y.) 1880-82. Ph.D., 1882. Professor of inorganic geology, Johns Hopkins University, Baltimore, Md. Died 1894.

Williams, W. J. 1869-70. Chief chemist at the Frankford Arsenal, Philadelphia, Pa.

*Wolff, Chas. (Cincinnati, Ohio.) 1863-65.

Wolf, Theo. R. 1868-70. Ph.D., 1870. Professor of chemistry, Delaware College, and State Chemist, Newark, Del.

Woodrow, James. 1856.

*Wright, Harrison. (Wilkesbarre, Pa.) 1869-70. Died 1885.

* Deceased.



Proceedings.

BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the Chemists' Club, 108 W. 55th St., New York City, Saturday, October 27, 1900.

The meeting was called to order at 9 o'clock P.M., by President McMurtrie. All the directors were present.

The minutes of all previous meetings were approved as recorded in the secretary's book.

The librarian was authorized to subscribe for the *Berichte* of the German Chemical Society.

It was voted that the president appoint a committee of two directors to whom should be referred the manuscript of the index prepared by Mr. Sohon, and the galley proof thus far prepared, and who shall examine into the question of errors submitted by the editor and report the same to the Board at its next meeting. Messrs. E. E. Smith and C. A. Doremus were appointed such committee.

The treasurer of the society was empowered to pay the necessary expenses for inserting funeral notices of the late Dr. E. R. Squibb in the daily papers.

The minutes of the meeting were read and approved and the meeting then adjourned.

ALBERT C. HALE, *Secretary*.

COUNCIL.

A local section of the Society for the benefit of those members who reside in and around Kansas City, Mo., to embrace those portions of the States of Missouri and Kansas included between the 93rd and 98th meridians, with headquarters at Kansas City,

Mo. (714 Wyandotte St.), was authorized by the Council, November 6.

NAMES PROPOSED FOR MEMBERSHIP.

Boesch, Basil W., 36 Union Park, Boston, Mass.
 Brown, C. Arthur, 630 W. 8th St., Cincinnati, Ohio.
 Burtt, Stratford, 840 Halsey St., Brooklyn, N. Y.
 Caspari, Chas. E., 312 W. 115th St., N. Y. City.
 Cathcart, Wm. K., Maywood, N. J.
 Chambliss, Hardee, 312 W. 115th St., N. Y. City.
 Cook, Alfred N., Sioux City, Iowa.
 Davis, Leon K., 185 Temple St., West Newton, Mass.
 Dodge, Francis D., 60 S. Oxford St., Brooklyn, N. Y.
 Dreyfus, Wolfram E., 175 W. 107th St., N. Y. City.
 Henius, Max, 290 S. Water St., Chicago, Ill.
 Hummell, A. S., Box 195, High Bridge, N. J.
 Hunter, Edwin E., 122 S. 3rd St., St. Joseph, Mo.
 Jordan, James O., 994 Washington St., Boston, Mass.
 Josephson, Edgar, 131 Amity St., Brooklyn, N. Y.
 Kingman, Wm. A., 55 Lincoln St., So. Framingham, Mass.
 Laws, Eugene H., 54 Kellogg St., Fall River, Mass.
 Mead, George H., Cellulose Products Co., Boston, Mass.
 Morgan, Leonard P., 4714 Chester Ave., Philadelphia, Pa.
 Owens, Wm. G., Bucknell Lab., Lewisburg, Pa.
 Patterson, G. W., Indian Head, Md.
 Roberts, Alfred E., 23 St. Botolph St., Boston, Mass.
 Robison, F. W., Columbus Ford Lab., 103 State St., Chicago,

III.

Shepherd, Earnest S., Remington, Ind.
 Sinkinson, Joseph D., 85 Willow St., Brooklyn, N. Y.
 Sparks, John C., Bement Ave., Livingston, Richmond Co., N. Y.
 Stieglitz, Julius, Univ. of Chicago, Chicago, Ill.
 Tingle, Alfred, Chem. Lab., Columbia Univ., N. Y. City.
 Tingle, John B., Lewis Inst., Chicago, Ill.
 Tolman, Lucius M., 1937 13th St., N.W., Washington, D. C.
 Trowbridge, Dic. H., Lewis Inst., Chicago, Ill.
 Waterhouse, James S., Cumberland Univ., Lebanon, Tenn.
 Wahl, Dr. Robert, 290 S. Water St., Chicago, Ill.
 Waters, Charles D., 6 Magnolia St., Roxbury, Mass.
 Waters, C. E., Conn. Agr. Coll., Storrs, Conn.
 Wesener, John A., Columbus Ford Lab., 103 State St., Chicago, Ill.
 Ulmer, George F., Arbuckle Bros., Sugar Ref., Foot of Pearl St., Brooklyn, N. Y.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Bernheim, Geo. B., 74 E. 79th St., N. Y. City.
 Hellon, Robert, 40 Lowther St., Whitehaven, Eng.
 Hildreth, Thomas F., 530 W. 123rd St., N. Y. City.
 Kaufman, G. Falk, 63 E. 74th St., N. Y. City.
 Lindsay, William G., 207 W. 81st St., N. Y. City.
 Moffatt, Miles R., Momaroneck, Westchester Co., N. Y.
 Page, Robert W., 527 Third St., Brooklyn, N. Y.
 Pickhardt, W. Paul, 1042 Madison Ave., N. Y. City.

ASSOCIATES ELECTED OCT. 12, 1900.

Braun, F. W., 501-505 N. Main St., Los Angeles, Cal.
 Hicks, Walter T., 300 S. Broadway, N. Y. City.
 Baxter, W. T., Rolla, Mo.

NEW MEMBERS ELECTED OCT. 12, 1900..

Johnson, Charles M., 701 Orchard St., Avalon, Pa.
 Rademacher, Hermann A., Box 243, Lawrence, Mass.
 Rogers, Herbert F., Provident Chem. Wks., St. Louis, Mo.
 Vosburgh, C. H., High School, Jamaica, N. Y.

NEW MEMBERS ELECTED NOVEMBER 19, 1900.

Balcom, Reuben W., Mass. Inst. Tech., Boston, Mass.
 Baltzly, Edwin B., Perth Amboy, N. J.
 Benedict, Francis G., Middletown, Conn.
 Braman, Winfred W., Durham, N. H.
 Breves, Rudolph, Rahway, N. J.
 Brown, John W., 126 Massachusetts Ave., Boston, Mass.
 Champion, E. C., Iola Portland Cement Co., Iola, Kans.
 Gordon, A. S., Oliver Iron Mining Co., Mountain Iron, St. Louis Co., Minn.
 Grainger, William E., Cranberry, Mitchell Co., N. C.
 Hemmings, Frederick J., 12 Pearl St., Boston, Mass.
 Heckerroth, William C., 3443 N. 18th St., Philadelphia.
 Heckman, J. Conrad, Larkin Soap Co., Buffalo, N. Y.
 Melcher, Arthur C., 58 Bowen St., Newton Centre, Mass.
 Morgan, W. C., Washburn College, Topeka, Kans.
 Osgyani, Arpad, 64 Orchard St., Astoria, L. I., N. Y.
 Pough, Francis H., 146 Hicks St., Brooklyn, N. Y.
 Walton, James H., Jr., Room 317, 126 Massachusetts Ave., Boston, Mass.
 Wheeler, Alwyn S., Chapel Hill, N. C.
 Woods, Chas. D., Orono, Me.

ASSOCIATES ELECTED NOVEMBER 19, 1900.

Cary, Edward A., Lafayette College, Easton, Pa.
 Felt, W. W., 9431 Normal Ave., Chicago.

Haskell, Albert A., Essex, Mass.

Howard, John J., 118 McKeen Hall, Easton, Pa.

CHANGES OF ADDRESS.

Belden, A. W., Tenn. C. I. and R. Co., Birmingham, Ala.
Bigelow, S. Lawrence, 1520 Hill St., Ann Arbor, Mich.
Blouin, R. E., care Sugar Planters' Expt. Sta., Honolulu,
Hawaiian Territory.

Chamberlin, W. E., 111 Water St., N. Y. City.

Cornelison, R. W., Bloomfield, N. J.

Corse, Wm., 26 Hendrie Ave., Detroit Mich.

Falkenau, L., 538 Sacramento St., San Francisco, Cal.

Fay, Irving W., 177 Woodruff Ave., Brooklyn, N. Y.

Fourneaux, E. A., 130 W. 84th St., N. Y. City.

Gallagher, Phil. C., care Boston Gold Copper Sm. Co., Lead-
ville, Colo.

Gallivan, F. B., 56 Prospect Place, Brooklyn, N. Y.

Granja, Rafael, Box 799, Kingston, R. I.

Gudeman, Edward, 4319 Vincennes Ave., Chicago, Ill.

Harding, Everhart P., Univ. of Minnesota, Minneapolis, Minn.

Harrison, J. B., care Harrison, Griffin & Co., Bridgewater
Place, Manchester, Eng.

Hart, Edwin B., care Frau Rothchild, 11 Steinweg, Marburg,
Germany.

Hinds, J. I. D., Univ. of Nashville, Nashville, Tenn.

Hopkins, Erastus, Lake Mary, Fla.

Jacobs, Chas. B., 44 Broad St., N. Y. City.

Keller, Edward, Box 724, Baltimore, Md.

Kendall, Arthur I., care Cinclare Cent. Factory, Cinclare, La.

Knight, Geo. W., 39 Front St., Schenectady, N. Y.

Kohr, D. A., 110 Huntington Ave., Boston, Mass.

Lazell, E. W., 1130 Walnut St., Philadelphia, Pa.

Logan, Miss Lily, Majestic Hotel, 72nd St. and 8th Ave., N.
Y. City.

Lyng, M. H., Union Bag & Paper Co., Sandy Hill, N. Y.

Miller, S. C., 929 New York Ave., N. W., Washington, D. C.

Mommers, Richard, care Glucose Sugar Ref. Co., Marshall-
town, Iowa.

Neilson, Thos., Silver Bell Camp., Redrock, Pinal Co., Ariz.

Neish, Arthur C., Columbia Univ., N. Y. City.

Nelson, E. K., 4220 Grand Boulevard, Chicago, Ill.

Parker, Francis L., Jr., Johns Hopkins Univ., Baltimore, Md.
du Pont, Pierre S., Lorain, Ohio.

Redpath, Leon W., 22 Catherine St., Newport, R. I.

Reuter, L. H., Rue de Mérode 17, Brussels, Belgium.

Rickards, Burt R., 607 Sudbury Bldg., Boston, Mass.

Riggs, G. W. 46 E. 29th St., N. Y. City.
 Rogers, Allen, 3605 Locust St., Phila., Pa.
 Saarbach, Ludwig, 114 Pearl St., N. Y. City.
 Sadtler, S. P., N. E. Cor. 10th and Chestnut Sts., Philadelphia, Pa.
 Sargent, Chas. L., Murphy Varnish Co., Newark, N. J.
 Schuyler, E. H., Erie High School, Erie, Pa.
 Sherrard, V. P., Bland, N. M.
 Shilstone, H. M., Miles' Planting & Mfg. Co., Burnside, La.
 Thompson, Firman, Bundaberg, Queensland, Australia.
 Van Gelder, A. P., Landing, N. J.
 Walker, Claude F., New Britain, Conn.
 Watson, E. T., 172 E. Main St., Chillicothe, Ohio.
 Willcox, F. A., The Oaks, West, Sunderland, Eng.
 Woolworth, James G., 11 Halsey St., Providence, R. I.

ADDRESS WANTED.

Emmens, Stephen H., formerly of 1 Broadway, N. Y. City.

MEETINGS OF THE SECTIONS.

NORTH CAROLINA SECTION.

The Fall meeting of the section was called to order in Crowell Science Hall, Trinity College, Durham, by the presiding officer, Prof. B. W. Kilgore, on November 9, 1900, at 8 P.M. Thirty members and visitors were present. The following papers were read and discussed:

"International Atomic Weights," by Charles Baskerville.

"The Soil Survey in North Carolina and the Practical Value of the Results," by C. D. Harris.

"Notes on the Adie and Wood Method for the Determination of Potassium," by Charles Baskerville and I. F. Harris.

"The Determination of Certain Organic Radicals," by Charles E. Brewer.

"Formaldehyde as a Preservative of Food Material and its Detection," by W. M. Allen.

"Richter and the Periodic Law," by F. P. Venable.

"The Basis of Scientific Thought," by Charles Baskerville.

"Kilgore's Modification of the Volumetric Method of Estimating Phosphoric Acid," by C. B. Williams.

Reduction Products of Dehydromucic Acid," by H. B. Hill and A. S. Wheeler.

"The Oxidation of Cellulose," by A. S. Wheeler.

"The Necessity for State Supervision of Escaping Noxious Vapors and Contamination of Streams from Manufacturing Enterprises," by Charles Baskerville.

"Some New Chromium Salts," by J. E. Mills.

"Exhibition of a Mechanism for Marking Calibrated Apparatus," by C. B. Williams.

"Individual Effort as a Factor in Organized Scientific Work," by B. W. Kilgore.

There being no further business the section adjourned.

C. B. WILLIAMS, *Secretary*.

NEW YORK SECTION.

The October meeting was held on the 5th at the Chemists' Club. The papers read were:

"Dr. Meyers' Tangent System of Sulphuric Acid Manufacture," by C. Glaser.

"Note on the Determination of Zinc in the Franklin, New Jersey, Ores by the Ferrocyanide Method," by William H. Bassett.

The Chair appointed the following Committee on Prizes: C. Richardson, P. de P. Ricketts, and M. Loeb.

M. T. BOGERT, *Secretary pro tem*.

The November meeting was held on Friday evening, November 9th, at the Chemists' Club.

The minutes of the previous meeting were read and approved.

A paper entitled "A Brief Review of Antipyrin and Its More Important Derivatives," was read by D. C. Eccles.

A motion was made to appoint a Committee on Papers. It was seconded and carried.

A motion to elect a vice-chairman was made and seconded, and the election proceeded with. M. T. Bogert was unanimously elected.

A motion to publish an annual report was lost.

The death of Dr. E. R. Squibb was formally announced and a brief sketch of his life by Dr. Charles Rice, was read by the chairman.

It was voted to appoint a committee to draft suitable resolutions expressing the Society's appreciation of Dr. Squibb's

character, of his services to chemical science, and of the loss sustained by his death; and that the said resolutions be engrossed in duplicate, a copy to be sent to his family and one to be preserved by the Society.

The meeting was then adjourned.

DURAND WOODMAN, *Secretary*.

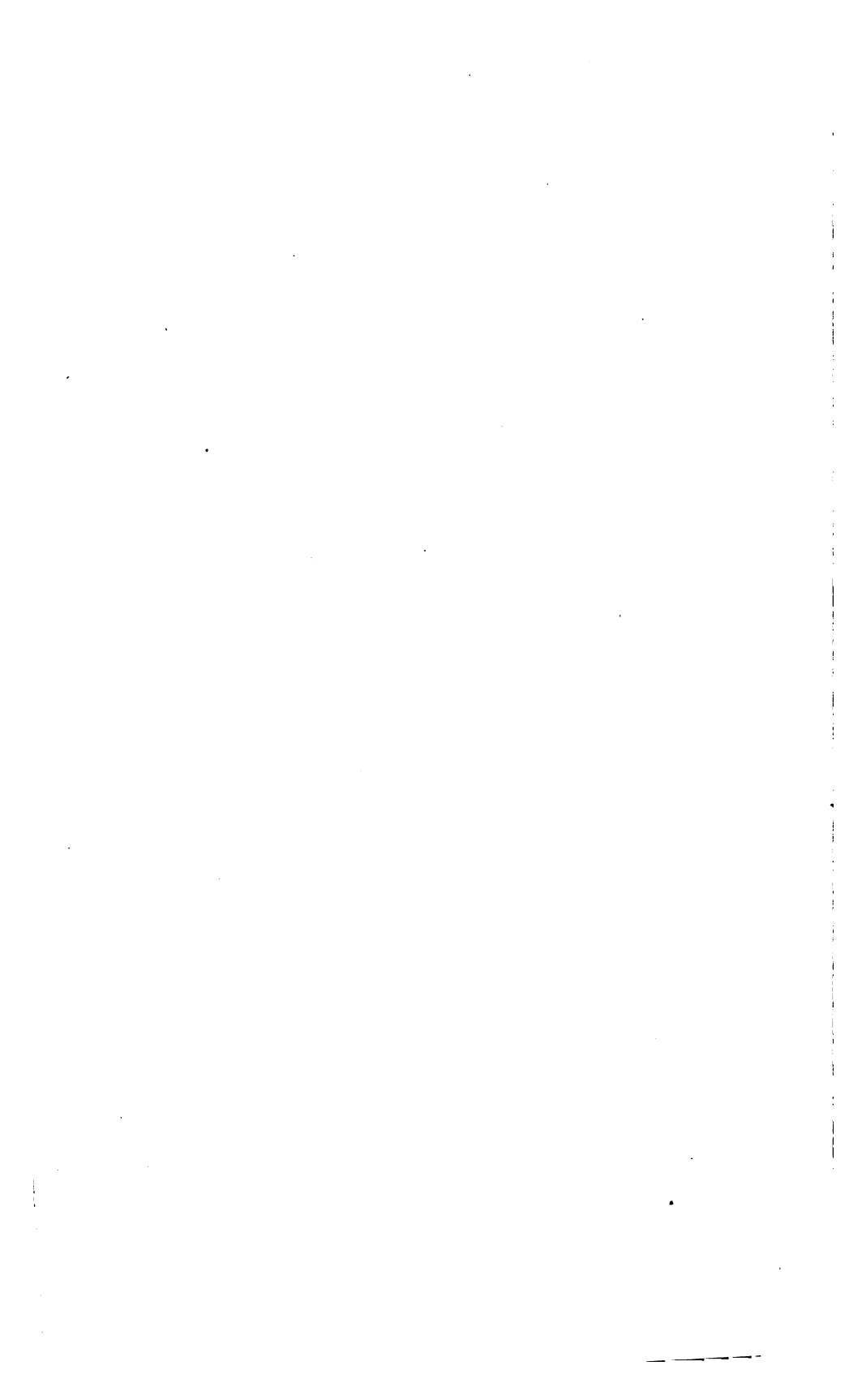
LEHIGH VALLEY SECTION.

A regular meeting of the Lehigh Valley Section was held at South Bethlehem, in the chemical laboratory of Lehigh University, on Thursday evening, October 18th. Resolutions were adopted relative to the establishment of a National Standards Bureau and of a Bureau of Chemistry in the United States Department of Agriculture to prevent the adulteration, etc., of food, after which the following papers were read:

"A Water-jacketed Crucible," by Dr. Porter W. Shimer; "Rapid Estimation of Sulfur in Iron," by Dr. Porter W. Shimer; "Valuation of Iron in Magnetite Ore by Specific Gravity Test," by Dr. Joseph W. Richards; and "A Method for Preparing Exactly Normal, Seminormal, Decinormal, etc., Sulfuric Acid," by Richard K. Meade.

The papers were discussed by Drs. Shimer, Richards, and Von Wachtel. In addition to the above, Dr. Richards who had just returned from Paris, entertained the section with a short interesting talk on the metallurgical exhibits at the Exposition.

RICHARD K. MEADE, *Secretary*.



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